

Report No. IITRI-C6014-8
(Triannual Report)

DEVELOPMENT OF SPACE-STABLE
THERMAL-CONTROL COATINGS
(PAINTS WITH LOW SOLAR ABSORPTANCE/
EMITTANCE RATIOS)

George C. Marshall Space Flight Center

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FOREWORD

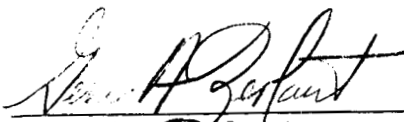
This is Report No. IITRI-C6014-8 (Triannual Report) of Project C6014, Contract No. NAS8-5379, entitled "Investigation of Environmental Effects on Coatings for Thermal Control of Large Space Vehicles." The report covers the period from September 20, 1963, to January 20, 1964. A previous Triannual Report was issued on October 25, 1964.

Major contributors to the program included Gene A. Zerlaut, Project Leader; Y. Harada and H. Rechter, inorganic coatings; Edwin H. Tompkins and Richard C. Reichel, microporous structures; Warren Jamison, space-chamber operation; and Douglas G. Vance, silicone paint preparation.

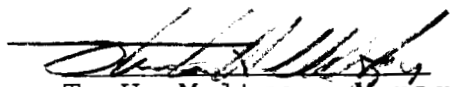
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Respectfully submitted,

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ABSTRACT

DEVELOPMENT OF SPACE-STABLE THERMAL-CONTROL COATINGS (PAINTS WITH LOW SOLAR ABSORPTANCE/ EMITTANCE RATIOS)

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The investigations of microbubble structures have indicated a great potential for this type of scattering system. A porous, methyl silicone coating with a solar absorptance of 0.11 has been formulated by leaching a finely divided salt from the silicone matrix with water. Thus, the real limitations to the use of microbubbles as scattering systems appears to be the stabilities which can ultimately be achieved with polymeric films. The principal problem currently being investigated is the possibility of enhanced degradation of the polymer matrix due to deep scattering of the ultraviolet radiation.

Pigment mixing studies employing zinc oxide and a secondary, ultraviolet-reflecting pigment were generally unsuccessful to improving the ultraviolet reflectance -- and thus the solar absorptance -- of corresponding paints. In some instances the secondary pigment not only failed to improve ultraviolet scattering but also had an adverse effect on the scattering of zinc oxide at longer wavelengths.

Overlayers of ultraviolet-reflecting paints appear to hold some promise for decreasing the solar absorptance of zinc oxide paints. The principal problem with topcoats such as zircon, zirconia, or Lithafax will be the competition between coatings thick enough to provide reflectance reinforcement in

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the ultraviolet and coatings thin enough not to detract significantly from the ultraviolet stability of the system.

Author

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I. INTRODUCTION

Studies during this report period have generally followed those outlined in the first Triannual Report, namely, (1) techniques to increase the ultraviolet reflectance of zinc oxide paints at little or no expense to their stability, and (2) techniques to maximize their reflectance in the remainder of the solar spectrum.

During the past few weeks we have placed greater emphasis on the investigation of microporous structures in polymeric films. In this respect, it is important to realize that micropores which provide broad-band scattering in the solar spectrum are the ultimate ultraviolet-stable, wholly transparent, and nonabsorbing pigment systems. The increased emphasis on the generation of microbubbles in coating films therefore appears highly profitable.

Also discussed in this report are pigment mixing studies, dual-layer coatings which employ ultraviolet-reflecting topcoats, and general considerations which affect the reflectance of pigmented systems.

II. DEVELOPMENT OF MICROPOROUS STRUCTURE IN PAINT VEHICLES

A. Introduction

The main objective of this phase is to make a coating from an ultraviolet-stable vehicle; the coating should have a bubble structure or some other variation in refractive index that will scatter ultraviolet and other wavelengths in solar radiation. In addition to bubble structures, we are also interested in polymer systems analogous to Teflon, in which light scattering results from variations in the degree of polymerization. Certain photographic processes involving vinyl polymers depend on such structures for image development. We are looking for ways of applying these principles to the comparatively ultraviolet-stable polydimethylsiloxane (silicone) resins.

If the vehicle containing bubbles or other structures is to be of any use for scattering ultraviolet radiation (and light of any wavelength), it must be transparent in the ultraviolet (or in the region of interest). Transmittance spectra for two silicones on quartz substrates were determined by using the Seya-Namioka 0.5-meter ultraviolet spectrometer. The curves shown in Figure 1 have been plotted as they came from the instrument without any reduction to % transmittance. The phenyl-methyl silicone absorbs below 2750 Å, but our experimental methyl silicone shows no cutoff at wavelengths longer than the limit of the quartz in the supporting substrate.

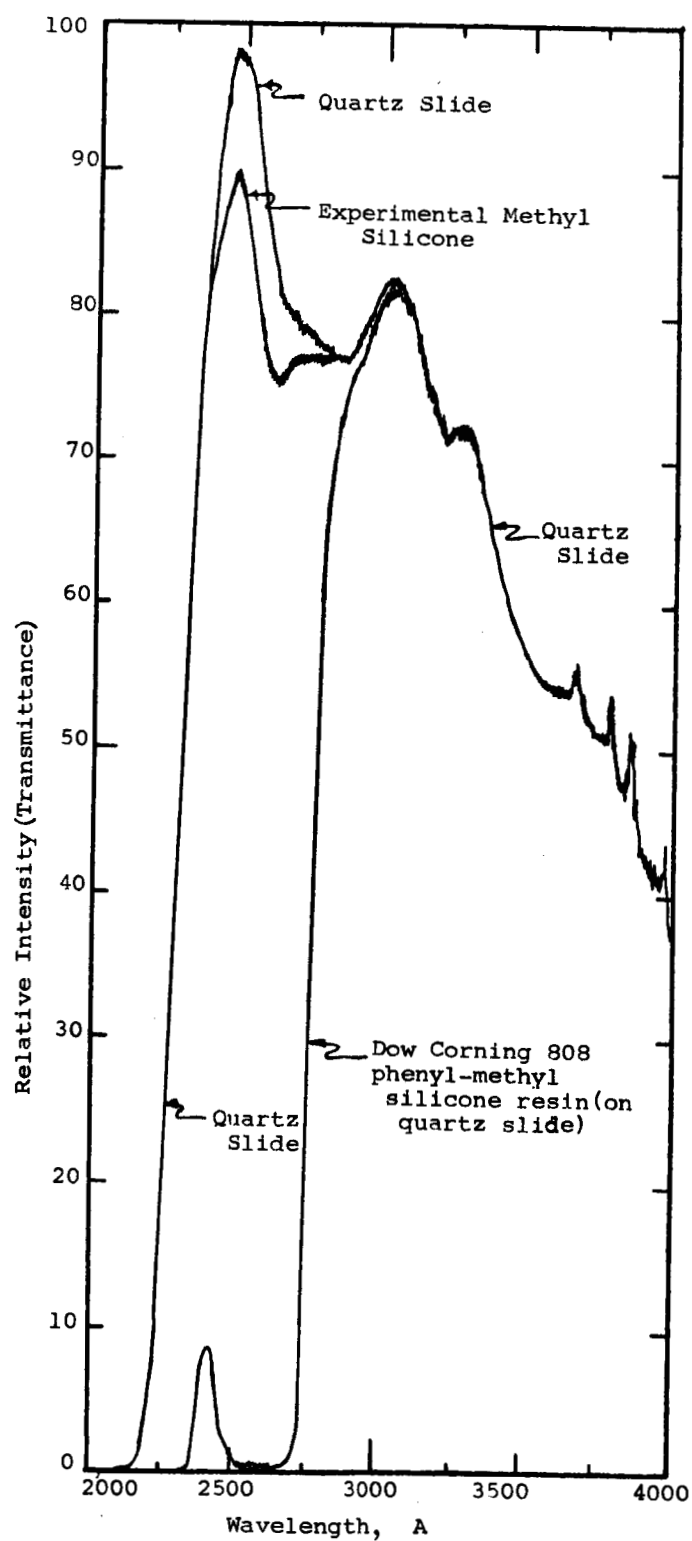


Figure 1

TRANSMITTANCE SPECTRA OF A PHENYL-METHYL AND
A METHYL SILICONE RESIN ON QUARTZ SUBSTRATES

A zinc oxide paint formulated from the experimental methyl silicone resin has been found to be one of the more stable white paints known.¹ If methyl silicones are reasonably stable to the ultraviolet of the space environment, they are an ideal medium for the suspension of bubbles for this work; this is the reason for our emphasis on silicone matrices. Unfortunately, there is the strong possibility that deep scattering of ultraviolet light by the microbubbles (or even by very "stable" ultraviolet-scattering pigments) will cause a considerably greater intensity of color (yellowing, etc.) compared to the amount observed when methyl silicone resins are pigmented with zinc oxide. Zinc oxide and other ultraviolet-absorbing pigments act as filters of ultraviolet light and quickly attenuate the radiation in the surface layers. Although damage due to ultraviolet irradiation in vacuum (and in air) is normally confined to the outermost layers (5-7 μ), the combination of ultraviolet scattering and the transparency of the silicone matrix might serve to enhance the process of darkening and coloration.

The problem of determining the extent to which deep scattering of ultraviolet light enhances the breakdown of the

¹Zerlaut, G. A. and Harada, Y., "Stable White Coatings". Report No. IITRI-C207-25 (Summary Report), Contract 950111, Jet Propulsion Laboratory, August 29, 1963.

methyl silicone vehicle is being investigated. Earlier in the program we irradiated a specimen of sodium silicate solution which had been foamed with hydrazine hydrate.² Irradiation in vacuum caused the specimen to turn coal-black. Therefore, it was concluded that residual hydrazine hydrate was present in the matrix and caused the blackening. Examination of the specimen revealed the possibility of precipitation of colloidal silica, which also could have influenced the degradation.

Subsequent irradiation of a foamed experimental methyl silicone, R-5, resulted in the same type of blackening. This material, foamed with methylene chloride, was cross-linked with a large excess of tetrabutoxy titanium (TBT) to rigidify the resin at temperatures low enough to retain the bubble structure. The TBT effectively cross-links the silicone by reacting with the residual pendent hydroxy groups of the dimethylsiloxane chains, creating a titanium-oxygen-silicon bond. Because of the tetrafunctionality of orthoesters of titanium, the use of the ester introduces many of these linkages. Titanium orthoesters, particularly those of the lower alkanes, like TBT, are hydrolytically unstable; TBT is

²Zerlaut, G. A., Tompkins, E. H., and Harada, Y., Report No. IITRI-C6014-4 (Triannual Report), Contract NAS8-5379, Oct. 25, 1963.

hydrolized to the hydrated titanium oxide by the moisture in air.

Therefore, even though we have not observed enhanced degradation of our zinc oxide-methyl silicone paints¹ by the use of small (1% based on resin solids) amounts of TBT, the use of a large excess could have caused the observed degradation. It is unlikely that any residual methylene chloride was left, particularly after several hours of evacuation before irradiation. In Figure 2 the reflectance of the foamed R-5 is plotted for two light sources in the Cary model 14 spectrophotometer. The upper curve was obtained with a hydrogen source, and it appears to contain luminescence bands. The lower curve was obtained with a standard incandescent tungsten source. The reason for the luminescence structure is not clear, and more work is planned. The silicone was on a glass substrate; therefore most of the reflectance was due to the bubble structure (a black backing was placed behind the glass slide during the reflectance measurements).

B. Commercial Foaming Techniques

Commercial foamed materials are not sufficiently stable in the ultraviolet to be used as spacecraft thermal-control coatings, but their techniques of preparation are applicable to ultraviolet-stable materials and their optical properties are those desired in foams for satellites. The following is a short summary of commercial foaming techniques with a bias toward the spacecraft-coating application.

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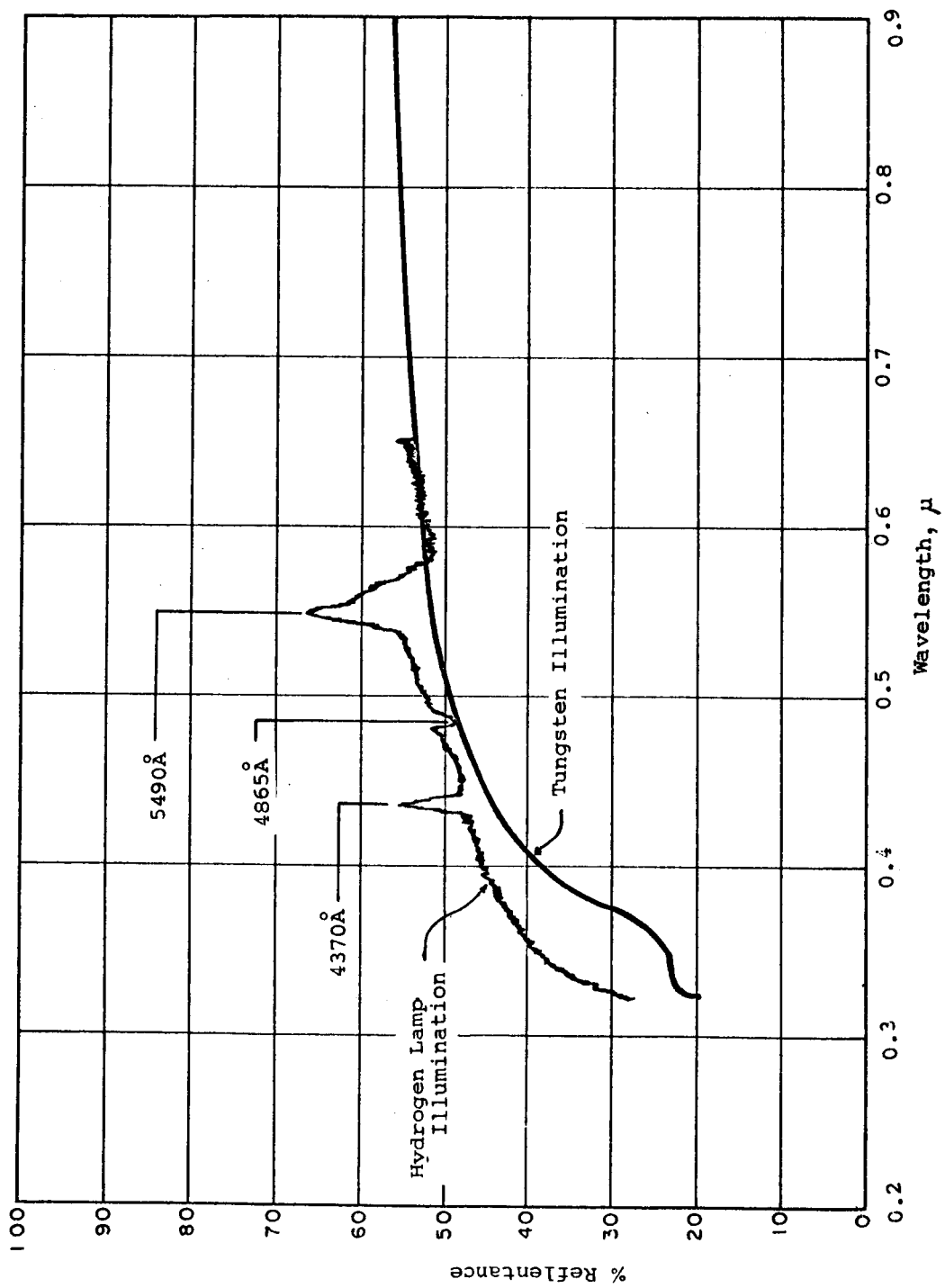


Figure 2
REFLECTANCE OF FOAMED RESIN R-5 AS A FUNCTION OF ILLUMINATION

Some foams are made by mechanical beating of carbon dioxide or other gases into an emulsion of the polymer. This method had been applied to vinyl and urea-formaldehyde resins, but for spacecraft materials the problem would primarily be to design the appropriate "beater" device. The mechanical method should not be ruled out, but other methods involving less equipment design have been given priority.

Volatile compounds, such as Freons, methylene chloride, pentane, propylene, and water, incorporated in polystyrene, polyethylene, and cellulose acetate generate foam structures when heated. Bubble size in this type of process is not easily controlled. For spacecraft materials the process is of interest because the blowing agents are either stable in solar ultraviolet or removed almost completely from the polymer during the foaming process. Thus we have given this method considerable experimental study in spite of control problems.

One technique of special interest consists of polymerizing a polymer around a water-soluble suspension and leaching out the soluble material after polymerization. This method offers maximum control of void size in a foam, but it yields a porous open structure. In a typical variation of the process, a soluble starch or salt is milled into a vinyl chloride monomer, and the dispersion is leached with water after polymerization. Battery separators and fine porous filter materials are produced by E.S.B.-Reeves by this technique. We have started

work on this type of foam, and considerable new work is planned. Techniques for sealing the open pore structure by volatile solvent-polymer foaming mixtures might be feasible.

Polyurethane foams are expanded by the reaction of isocyanate end groups with water. Somewhat similar reactions which are more likely to be useful in space coatings include the reaction of metal powders or sodium bicarbonate with acids generated by polymerization or by the addition of acids to the system. This type of reaction may not be as sophisticated as other methods, but at least in the case of metal powders there is the possibility of close control of bubble size in the foam.

Among the many chemical blowing agents available for the thermal generation of nitrogen bubbles in polymers, the three listed in Table 1 are of most interest here because of the characteristics of the decomposition products. Many diazo compounds and other nitrogen compounds readily yield gases on heating, but they are unsuitable for stable white coatings because they either yield colored decomposition products or they form products which are easily degraded by ultraviolet light.

Nitrogen gas can be generated from many diazo compounds by exposure to ultraviolet light or violet-blue light. This photolysis mechanism is the basis for the Kalvar photographic process and for the bleaching step in the Ozalid process. In

Table 1
SELECTED CHEMICAL FOAMING AGENTS

Chemical Name	Trade Names	Structure	Decomposition Temp., °C (in plastics)
Azobisformamide	Kempore Celogen AZ Genitron AC Porofor K- 1074	$\text{H}_2\text{NCO-N=N-CONH}_2$	160 - 200
Azobisisobutyro- nitrile	Genitron AXDN Porofor N	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{NC}-\text{C}-\text{N}=\text{N}-\text{C}-\text{CN} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	105 - 120
Diazoaminobenzene	DAB Porofor DB	$\text{C}_6\text{H}_5-\text{NH-N=N-NH-C}_6\text{H}_5$	95 - 100

the early stages of this work we tried the Kalvar process, but the colors of the original materials and decomposition products precluded any extended research. The Kalvar process demonstrates well, however, the fact that small bubbles of nitrogen are lost very rapidly from a polymer when it is overheated. The micron-size bubbles in the gelatin Kalvar film disappear rapidly (probably by moving to the outer surface of the film) when the film is overheated slightly. This observation accounted for the many difficulties we encountered later with small bubbles in films that were too soft to retain the bubble structure. The silicones with the greatest ultraviolet stability yield polymers which are not the best structures for stable micron-size bubbles.

As a final comment in this background discussion we should mention that a number of commercial silicone foams have been made by using N-nitroso compounds (Unicel ND, Du Pont). The mixture of silicone, catalyst, and blowing agent is heated to 320°F to generate the bubble structure.

C. Experimental Work

The experimental work on this phase of the program has been divided into two main areas: (1) the determination of the reflectance spectra of commercial foams and the extension of the results through simple theory to finer foam structures, and (2) the duplication and development of techniques for making practical foam structures. The second area has received the most attention.

1. Reflectivities of Commercial Foams

Van De Hulst³ points out that the optical frequencies and scattering equations for spherical cavities are similar to those for solid spheres but that they cannot be readily reduced to each other. As far as the present work is concerned, the main point is that strong scattering will occur when the diameter of a cavity is comparable to the wavelength of the light inside the cavity. Since few available

³Van De Hulst, H. C., Light Scattering by Small Particles, John Wiley, 1957, p. 155.

materials contain high concentrations of cavities of such small size, much of the work on this program has been directed toward the practical problem of producing such fine bubble structures. Even from coarse commercial foams, however, one can get an idea of the potentials of microfoam scattering. In this report spectral reflectance results for several commercial foams are compared with micrographs of the bubble sizes and structures.

The photomicrographs in Figure 3 show the structures of four commercial products. The following are brief descriptions of these materials.

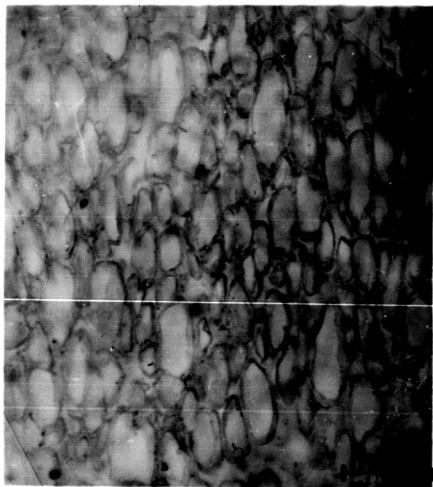
Micrograph a is a polyvinyl chloride material,

Micropore, made for filtration. The polymer is polymerized around starch particles, and these particles are leached out with water. Continuous channels run through this material.

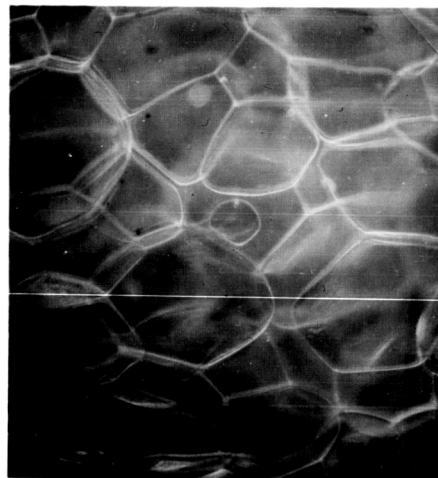
Micrograph b is a polystyrene-sheet foam expanded by a volatile solvent. The sheet has been rolled, and the bubbles are flattened in the plane of the photograph. The walls of the plastic between the bubbles are unusually thin. The orientation by rolling gives the sheet a sheen characteristic of multiple layers of thin platelets.

Micrograph c is a coarse polyurethane foam.

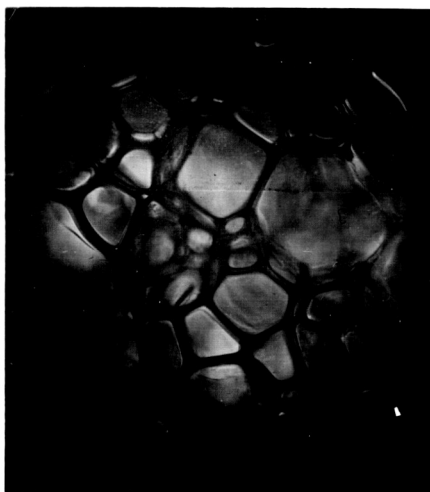
Micrograph d is expanded polystyrene bead material used in packing chemicals, etc. The bubbles lack



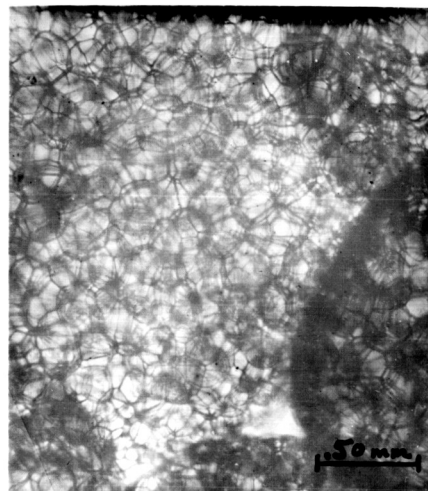
a. Polyvinyl chloride



b. Polystyrene sheet



c. Polyurethane foam



d. Polystyrene bead

Figure 3

PHOTOMICROGRAPHS OF COMMERCIAL FOAMS

the laminar orientation of the sheet in micrograph a.

The reflectances of the four commercial foams are plotted in Figure 4. The curves are labeled a through d to correspond with the notation used for the micrographs in Figure 3. Curve a is the foamed polyvinyl chloride known as Micropore. It will be noted that this material possesses the highest reflectance of the four foams. From Figure 3 it can be seen that it also possesses the smallest pore size of the four materials. The Micropore is foamed by the dispersion of solid sized starch particles and the subsequent leaching out with water after the polymer has been rigidified. The solar absorptance of the Micropore specimen was computed from curve a as 0.12 after accounting for the reflectance of the magnesium oxide standard.

Curve b is the reflectance of a low-density, unsupported foamed polystyrene about 1 mm thick. The pores in this material are small compared to materials c and d, but under microscopic examination they were to have a mean diameter of about 100 μ , a dimension much in excess of visible wavelengths. These pores are separated by thin membranes of the plastic. In other words, much of the scattering in this material results from multiple reflection at film surfaces.

Curve c is the reflectance of a coarse polyurethane foam with the largest pore size of the four commercial materials. Curve d, the middle curve in Figure 4, was also obtained from a polystyrene foam (such as used to pack acid bottles), but

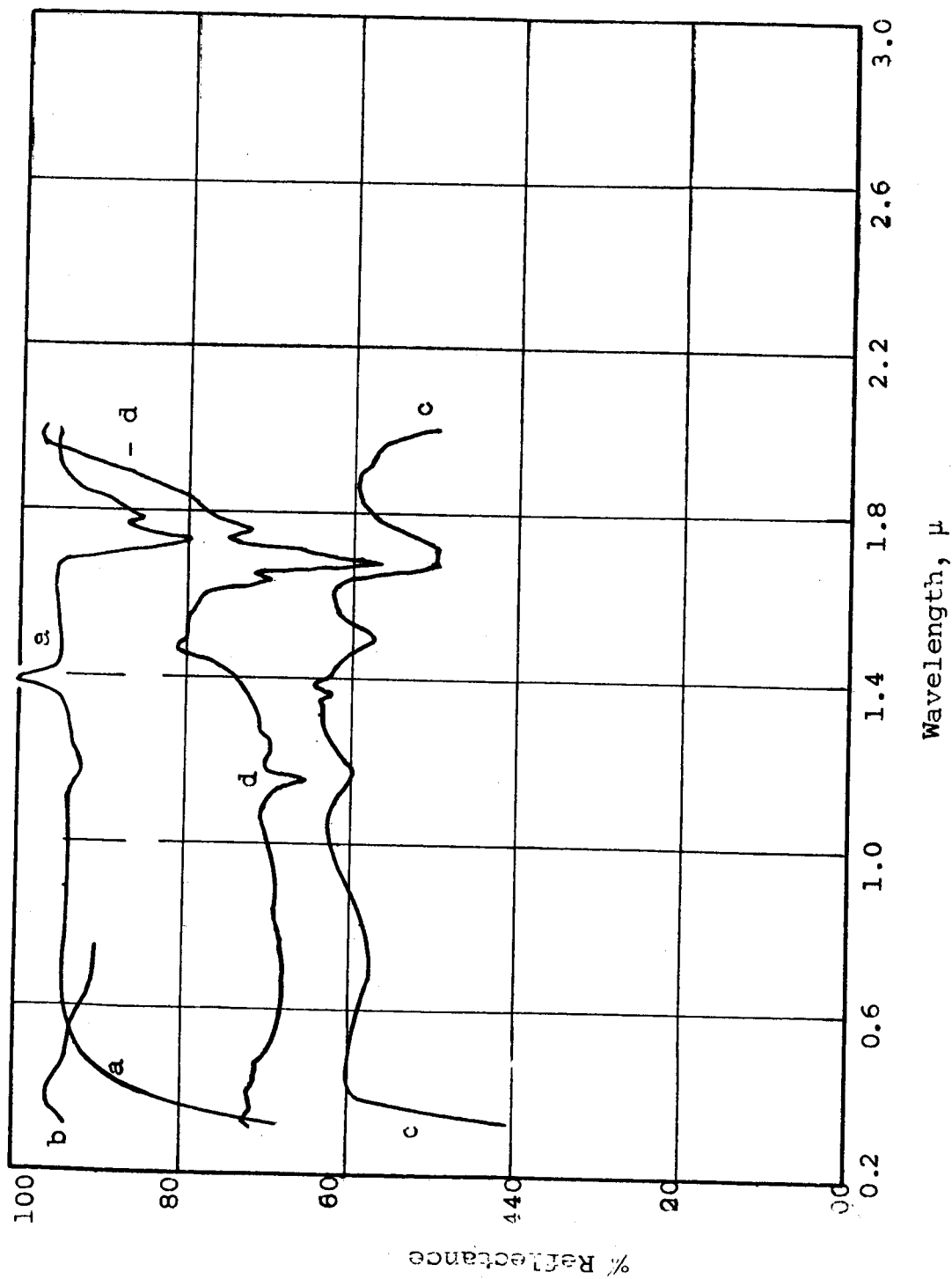


Figure 4

REFLECTANCE OF COMMERCIAL FOAMED POLYMERS

the foam structure was less ordered and compact than in the polystyrene sheet, b. The pore sizes are about equal in both cases, but the second material, d, was made by compacting pellets of foamed polystyrene into a mold. This method of preparation results in many deep open pores and cracks, which allow the light to penetrate far into the sample before it starts to scatter. The effect of this geometric structure is much more pronounced in the spectrometer than might be expected from visual observation. Both materials were compacted near the surface under pressure from rolls or a mold, and it is apparent that alignment of the walls of the pores relative to the front surface of the sample is an important factor. Each pellet of foamed material in the second sample was separated by a visibly less reflective boundary. Presumably the area between the pellets was occupied by a high proportion of pore walls oriented roughly perpendicular to the front surface of the sample.

2. Reflectivities of Experimental Foams

A review of experiments to prepare foamed silicone and foamed sodium silicate in the laboratory is presented in Table 2. The reflectance of three selected specimens is presented in Figure 5. Specimen 121-1 (1 min at 240°F) possessed rather large bubbles -- a fact which is apparent from the reflectance curve. Specimen 124-2 (1) was prepared from sodium silicate using Poro for N and was heated for 15 min at 190°F. The rather unusual reflectance curve would

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Table 2

BUBBLE FORMATION

Sample No.	Treatment	Observed Results
<u>121-1</u> 50 g SR-80 0.5 g Porofor N (applied to glass slides)	None	Blowing agent appears to be well dispersed in the resin. The glass slide appears like a frosted window.
	8 min, 130°F	Very fine bubbles generated, and the coating is whiter.
	5 min, 200°F	Same as 180°F treatment above; however, some of the bubbles appear to extend from the top to the bottom of the coating.
	1 hr, 200°F	Very coarse, large bubbles generated. Coating is transparent rather than white.
	105 sec, 245°F	Surface is whiter than previous samples; however, there are a few coarse bubbles at the surface. The surface adjacent to the glass slide has much larger bubbles that are not visible from the upper surface.
	1 min, 240°F	Sample whitened and is quite similar to 200°F-5 min test above in that some of the bubbles appear to extend from top to bottom of the coating. One edge, which has a thicker coating, appears to be whiter than the remainder of the sample. (Reflectance measured, Figure 5.)
	1 min, 240°F, cooled and 1 min, 240°F	Sample behaved the same as 240°F-1 min test above. After removal and reinsertion into oven for an additional minute, the sample became whiter, but more large bubbles resulted.
	30 sec, 280°F	Similar to 240°F-1 min test, but whiter in areas of apparently greater thickness. A few larger size bubbles on the surface.
<u>121-2</u> 5.0 g SR-83 0.3 g Porophor N	1 min, 280°F	Much better than 30-sec test above. Surface adjacent to glass slide has very coarse bubbles; however, the upper surface is composed of very fine bubbles.
	None	Coated slide did not appear as frosted as initial 121-1 coating. Coating looks like a slightly pebbled surface with occasional white specks.
	15 min, 200 °F	No whitening. Coating appears clear and the surface is smoother (leveled out).
	15 min, 230°F	Same as 200°F-15 min test.

Table 2 (cont.)

<u>Sample No.</u>	<u>Treatment</u>	<u>Observed Results</u>
<u>121-4</u> 5.0 g SR-80 2.0 g toluene 2.0 g methylene chloride 0.5 g Porofoor N	None	Intermittent areas with small white particles. Also many needle-like areas that also indicate precipitation and subsequent grain growth of the blowing agent.
	7 min, 200°F	Bubbles formed; however, they are too large.
	5 hr, 200°F	Solid clear film. All bubbles escaped.
	5 min 210°F	Some general whitening due to small bubbles.
	10 min, 210°F	Bubbles larger than 5-min test above.
	2 min, 240°F	White surface, many fine bubbles. Variation in coating thickness was noted.
	90 sec, 260°F	Similar to results of 210°F-5 min test. Bubbles slightly larger.
	1 min, 270°F	Similar to 240°F-2 min test. Bubbles are slightly larger.
	50 sec, 280°F	Same as 270°F-1 min test in areas where there was sufficient coating.
	1 min, 280°F	White surface on removal from oven. However, bubbles continued to coalesce and the whiteness diminished due to formation of very large bubbles.
<u>124-2</u> 20 g sodium silicate 1 g Porofoor N	None	Frosty window effect. Very small cracks on the coating surface.
	15 min, 190°F	Surface whitened. A few small bubbles centered from the top to bottom of the coating. (Reflectance measured, Figure 5).
	6 min, 210°F (2 coats of the solution)	Surface whitened and entrapped blowing agent (and most likely water as well) caused a ballooned surface that eventually collapsed, leaving a wrinkled surface.
	10 min, 210°F (three thin coats allowed to dry between coats)	Excellent whitening effect. Surface has some cracks. (Reflectance measured, Figure 5).
	1 hr, 180°F (three thin coats allowed to dry between coats)	White surface with no cracks. Very good specimen.

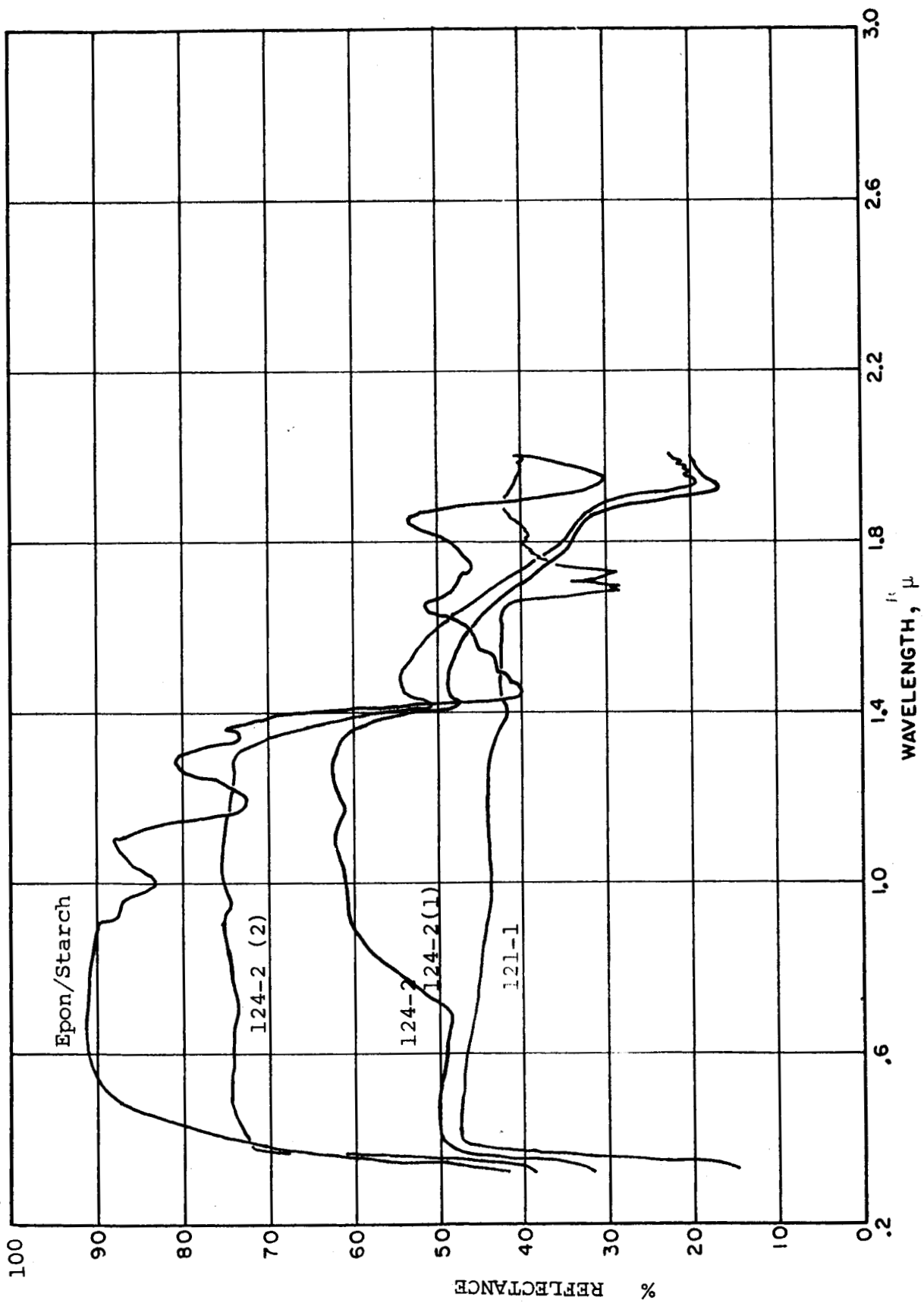


Figure 5
REFLECTANCE OF EXPERIMENTAL FOAMS

indicate a bimodal pore size distribution. The specimen described as 124-2 (2) was prepared from the same materials but heated for 1 min at 240°F. The structure at 1.4 μ cannot be explained although the general falling off of the reflectance of both specimens beyond 1.4 μ is attributed to an insufficient concentration of larger pores.

The top curve in Figure 5 was prepared by blending tapioca starch into an epoxy resin. Unfortunately, the entire material disintegrated in an attempt to leach out the starch by soaking in water.

Figure 6 shows the reflectance curves for a sodium chloride-loaded SR-80 silicone both before and after leaching with water. Curve A is the unleached specimen prepared by blending 10 parts/weight SR-80 with 14 parts of salt. Curve B is the same specimen after leaching with water. It will be noted that leaching improved the reflectance slightly at wavelengths longer than 0.6 μ ; below this a decrease was actually recorded. These specimens, like those above, were measured on a glass substrate backed with black cloth. The solar absorptance of the leached sample (B) was computed to be 0.11, indicating that this process holds much promise as a means of introducing microporosity into solid polymers. As noted earlier, the Micropore polyvinyl chloride filtration material was made by leaching starch from the cured polyvinyl chloride film. One problem we expect to encounter is difficulty in leaching the silicone films.

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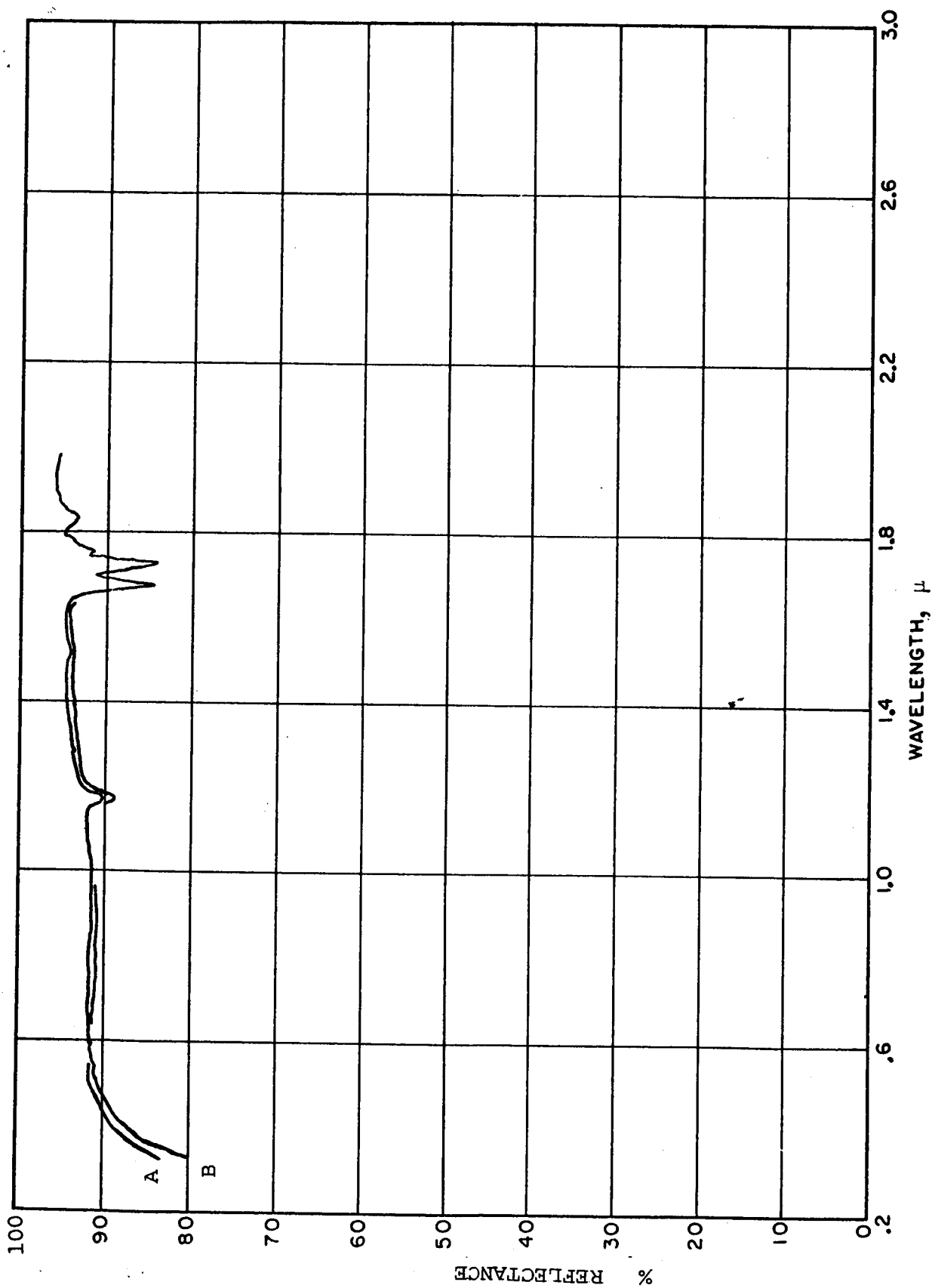


Figure 6
REFLECTANCE OF SODIUM CHLORIDE-LOADED SR-80 SILICONE

D. Discussion of Scattering in Geometric Systems

We have discussed some of the scattering mechanisms in the two polystyrene materials. In these coarse foams the orientation of the walls of the pores relative to the incident light is an unusually important parameter. If most of the membranes were oriented parallel to the light rays, their reflection would be poor. Membranes stacked with their surfaces perpendicular to the incoming light would reflect rather efficiently, like a pile of microscope cover glasses.

In these foam layers, it is evident that three types of scattering are involved.

1. Multiple reflection at membrane surfaces, as already mentioned.
2. Scattering by unevenness in the bubble walls and by islands of polymer between the bubbles.
3. Mie scattering by submicron bubbles with diameters comparable to the wavelengths of the light involved.

The bubbles provide one type of variation or discontinuity in refractive index, from 1.0 to 1.5, throughout the medium. Other sources of variation, such as different degrees of polymerization and different concentrations of polymer in a solvent, are also possible and are of considerable interest on this program. A photographic process patented by Gerald Oster (Brooklyn Polytech) depends on the separation of photopolymerized vinyl polymers from solutions of the respective monomers. This

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separation produces a white pattern corresponding to the light image in the film. We are studying possible ways of duplicating this process in ultraviolet-stable silicones and other materials.

The scattering mechanism for curve b in Figure 4 was mainly composed of mechanisms 1 and 2. Reduction of the bubble size to half in this material will reduce the mean path length of the scattered light in the plastic to about half. Since the energy absorbed is proportional to the mean path length for small degrees of absorption, the difference between the reflectances in the top curve of Figure 4 and 100% will be cut in half by such a reduction. If the system is scaled down to the point where Mie scattering predominates, this extrapolation breaks down; but even from this crude analysis it is apparent that high reflectances are possible. In fact, this mechanism appears to offer the only ultimate practical coating system for the thermal shielding of infrared detectors and low-boiling fuels in space.

E. Summary of Microporous Structures Studies

With our present catalysts and thermal curing cycles, the methyl and phenyl-methyl silicones are not sufficiently rigid during gas evolution (as a result of the blowing agents we have used to date) to yield small bubbles. The bubbles usually flow to the surface or coalesce before the silicone becomes rigid. This problem is a general difficulty in small-bubble foam manufacture. It is usually solved in part by decomposing or evaporating the blowing agents under

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pressure; we are trying to entrap small particles in insoluble blowing agents in fully polymerized epoxides, polystyrene, and silicones before heating to produce the gas. In general, our objective is to generate bubbles in polymers that are too rigid rather than too soft. It is easy to reduce the viscosity of a polymer; thus any difficulties with bubble matrices that are too hard can be remedied easily.

III. INORGANIC COATINGS

A. Pigments Study

The work for this period included studies of various white materials as potential secondary pigments in a zinc oxide-silicate system. Their prime purpose would be to increase the reflectance in the near-ultraviolet region, the area in which zinc oxide exhibits strong absorptance, limiting its solar absorptance (α) to about 0.12.

A number of white powders were pressed into compacts and examined in the wavelength region 0.325 μ to 2.0 μ in a Cary spectrophotometer. The measured values are tabulated in Table 3. The various materials are divided into four groups: Group I includes those which show high reflectances throughout the spectrum; Group II are those which are good ultraviolet and visible reflectors but which show poorer values in the infrared region; Group III are good infrared reflectors but relatively poor reflectors in the near ultraviolet; and

Table 3
SPECTRAL REFLECTANCE OF VARIOUS MATERIALS

Sample No.	Material	% Reflectance*									
		Wavelength, μ									
		0.325	0.375	0.450	0.600	0.700	1.0	1.2	1.4	1.6	2.0
1	ZnO	4	5	98	98	99	98	99	>100	99	99
Group I											
19	$\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$	100	100	100	100	>100	99	100	>100	>100	99
34	Al_2O_3	93	97	98	93	98	96	97	>100	97	97
15	LiF	95	96	97	97	97	97	98	>100	98	93
25	K_2SiF_6	92	95	96	96	96	95	95	94	96	93
4	BaP_2O_6	90	98	98	98	97	96	97	100	97	90
9	$\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$	96	97	97	97	97	95	96	100	93	84
20	Sodium Tripolyphosphate	83	96	98	93	98	98	99	>100	97	89
12	BaF_2	81	90	97	99	99	98	98	99	95	84
Group II											
7	GeO_2	>100	>100	>100	>100	>100	98	89	81	74	47
31	BPO_4	88	89	91	94	96	95	96	96	89	73
11	BaSO_4	100	>100	>100	100	100	94	90	78	63	38
22	$\text{LiBO}_2 \cdot \text{H}_2\text{O}$	87	89	93	95	95	90	91	85	62	50
24	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	91	92	95	97	97	92	86	80	75	43
11	BaSO_4	91	93	96	96	95	90	86	71	66	25
29	$\text{Na}_2\text{WO}_4 \cdot \text{H}_2\text{O}$	89	93	97	97	97	90	83	80	52	20
13	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	89	94	98	99	99	93	89	76	59	32
17	$\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$	76	98	>100	100	100	91	84	70	49	17
18	MgP_2O_6	77	90	94	96	97	92	89	81	51	35
Group III											
6	Ta_2O_5	72	88	92	96	97	97	99	>100	100	99
14	HgCl_2	54	82	90	93	94	95	97	>100	98	100
33	TeO_2	32	78	93	97	98	97	98	100	95	86
Group IV											
27	$\text{BaOH} \cdot 8\text{H}_2\text{O}$	75	78	88	99	99	97	98	94	93	74
21	$\text{Zr}(\text{OH})_4$	54	77	82	94	95	93	93	77	76	53
13	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	67	73	78	85	87	80	73	56	25	9
26	$(\text{NH}_4)_2\text{SiF}_6$	59	71	84	85	79	80	70	76	38	5
2	$(\text{NH}_4)_6\text{W}_{12}\text{O}_{42} \cdot 6\text{H}_2\text{O}$	14	78	93	98	98	91	85	75	46	26
30	$(\text{NH}_4)_6\text{Mo}_{10}\text{O}_{34}$	8	48	94	96	95	85	77	70	39	21

*versus magnesium oxide.

Group IV contains those materials which are comparatively poor in the overall region studied.

The studies revealed several materials that have excellent reflectances, noticeably those in Group I. Phosphates as a group appear to be extremely white; however, space simulation experiments conducted on a different program¹ have shown other phosphate materials to be degradable. The fluorides also are highly reflective. The use of these types of compounds in a silicate system to produce highly reflective coatings is hampered by the coincidence and proximity of refractive indices.

Despite their indicated infrared absorptance, Group II materials are also potential materials for lowering the solar absorptance of the zinc oxide-silicate system. This was indicated by topcoat experiments described later in this report. A zirconia topcoat improved the ultraviolet reflectance of a zinc oxide-silicate coating and retained the superior infrared reflectance of the latter.

The possibility exists that there may be other materials which are as stable as zinc oxide. Earlier work¹ has shown that in general, natural-mined minerals were less affected by ultraviolet irradiation in vacuum than synthetic laboratory

chemicals. Also, calcination of hydrated materials to their anhydrous state enhanced stability. An experiment is now being designed to determine the stability of an array of materials. The criteria will be high reflectance and high refractive index (or possible low in order to obtain a departure from that of potassium silicate); emphasis will be placed on natural compounds such as clays. Also to be investigated are some of the more exotic materials such as rare earth oxides; Cutright⁴ has shown that dysprosium oxide is relatively stable. Carbides, borides, nitrides, titanates, and spinels may also receive scrutiny.

B. Paints

Various pigments were incorporated into zinc oxide-silicate formulations in various amounts in an attempt to upgrade the ultraviolet reflectance. Secondary pigments were added to the mix before ball-milling; all paints were applied on glass substrates by spraying with an air brush, and curing was accomplished by air-drying only. Optical measurements for various combinations are shown in Table 4.

The results show that merely adding a secondary pigment has a limited effect on lowering solar absorptance. The improvement in low-wavelength reflectance was quite slight,

⁴Cutright, R. C. "Rare Earth Oxide for High-Temperature Reflecting Pigments," Presented at ACS, Division of Organic and Plastics Chemistry, NYC Meeting, September 1963, Vol 23, No. 2.

Table 4
SPECTRAL REFLECTANCE OF VARIOUS ZINC OXIDE-SILICATE PAINTS
CONTAINING SECONDARY PIGMENTS

Sample No.	Secondary Pigment Material	% Wt.	Thickness, mils.	PBR	% Reflectance*										
					0.325	0.375	0.450	0.600	Wavelength, μ	1.0	1.2	1.4	1.6	1.8	2.0
16-19	None		5.0	4.30	3.0	5.0	97.0	98.5	98.0	96.5	97.0	98.0	95.0	91.0	86.0
7-7	ZnS	12.5	5.0	4.30	0.0	5.0	95.0	96.5	84.5	94.0	94.0	93.5	88.0	81.0	76.5
7-15	ZnS	50.0	5.5	4.30	2.0	19.0	94.0	95.5	75.0	95.5	94.0	89.0	84.0	82.0	77.0
8-5	ZrO ₂	12.5	5.5	4.30	2.0	3.5	96.5	97.0	96.5	94.0	94.0	96.0	90.0	83.0	75.0
8-13	ZrO ₂	50.0	3.5	4.30	7.0	8.0	94.5	93.5	92.5	89.5	89.0	91.0	86.0	80.0	72.0
8-21	SnO ₂	12.5	4.0	4.30	1.0	4.0	94.0	96.0	97.0	96.0	96.0	98.0	90.5	84.0	76.0
8-30	SnO ₂	50.0	6.5	4.30	9.0	17.5	94.0	94.0	96.5	96.0	96.0	97.0	91.5	85.5	78.0
9-8	Dicalite**	12.5	8.5	4.30	6.5	7.5	89.0	93.0	93.0	91.5	92.0	94.0	89.0	83.0	76.0
9-13	Dicalite**	50.0	6.5	2.15	10.0	11.0	85.0	88.0	88.0	86.5	89.0	84.0	84.0	79.0	72.0
9-18	Calite**	50.0	12.0	2.15	18.5	18.5	93.0	95.0	94.5	93.5	94.0	95.5	80.0	83.0	74.5
9-21	Mg(OH) ₂	56.0	14.5	4.30	23.5	21.5	93.0	94.5	94.0	91.0	91.0	87.0	85.0	77.5	64.0
9-26	Al ₂ O ₃ ·3H ₂ O	50.0	9.0	4.30	2.0	3.0	86.0	92.5	93.0	90.0	91.0	80.0	80.5	76.0	65.0
10-1	LiAlSiO ₄	50.0	8.0	4.30	3.5	4.0	89.5	94.0	93.5	91.5	92.0	94.0	87.5	80.5	71.0
10-6	ZrSiO ₄	50.0	3.0	4.30	5.0	5.0	84.0	91.0	91.0	88.0	87.5	83.0	82.0	73.5	62.0
10-7	CaSiO ₃	50.0	4.0	4.30	2.5	3.5	88.0	89.5	89.0	86.0	85.5	88.0	83.0	78.5	71.5
13-1	BaP ₂ O ₆	50.0	9.5	4.30	5.0	5.0	91.5	93.5	93.0	91.0	91.5	91.5	84.0	73.0	60.5
13-4	Na ₂ B ₄ O ₇ ·10H ₂ O	33.3	6.0	3.20	21.5	18.0	90.0	88.0	86.5	84.0	84.0	86.0	82.5	81.0	73.5
13-12	Zr(OH) ₄	33.3	13.0	4.30	12.5	13.0	92.0	94.0	94.0	93.0	93.5	93.0	86.0	78.0	67.0
13-20	Ta ₂ O ₅	33.3	4.0	4.30	6.5	6.5	88.5	87.0	85.5	83.0	82.5	84.0	79.0	73.0	64.5
13-25	MgHPO ₄	20.0	10.0	2.15	21.5	20.0	95.0	93.5	92.5	90.5	90.0	89.5	80.5	67.5	55.0
13-29	AlPO ₄ ·2H ₂ O	20.0	7.0	2.15	4.0	4.0	90.0	88.5	87.0	84.0	83.0	83.0	73.5	61.0	45.0
15-1	Cb ₂ O ₅	20.0	5.0	2.65	5.0	9.0	92.5	92.0	91.0	89.0	88.5	90.0	82.5	74.0	62.5
15-5	AlF ₃	20.0	8.0	2.65	6.5	7.5	94.0	95.0	95.0	93.0	94.0	95.0	89.5	82.0	73.0
15-25	Na ₂ WO ₄ ·2H ₂ O	20.0	4.0	2.65	3.5	4.0	83.5	83.0	87.0	84.0	84.0	86.0	79.5	73.0	59.0
15-41	MgF ₂	20.0	11.0	2.65	5.5	6.5	92.0	93.0	92.0	90.0	90.0	91.0	84.0	76.0	66.5
15-45	LiBO ₂ ·5H ₂ O	20.0	3.0	2.65	3.0	3.5	78.0	74.0	73.0	69.0	68.0	69.5	65.0	61.0	52.0
16-16	LaF ₃ ·xH ₂ O	12.5	4.5	4.30	3.5	5.0	97.0	97.0	96.0	94.0	94.5	97.5	92.5	83.0	81.5

*versus magnesium oxide

**diatomaceous earth.

never exceeding 20% at wavelengths of 0.325 and 0.375 μ . Furthermore, in many cases the slight ultraviolet improvement was offset by reflectance losses in the visible and infrared. Thus, more sophisticated methods for utilizing the better optical properties of additives appear necessary.

C. Ultraviolet-Reflecting Topcoats

Attempts were made to improve the reflectance of a zinc oxide-silicate system by application of an ultraviolet reflecting topcoat. A zirconia-silicate formulation with a pigment-to-binder ratio (PBR) of 4.30 was brush-painted on a portion of each of three 1 x 3-inch zinc oxide-silicate samples. The topcoated portions are denoted with the suffix B in Table 5. Sample 1-B received a heavy topcoat, adding about 1.5 mils to the total thickness with a weight gain of 0.266 g. Thinner coats were applied on samples 2-B and 3-B; the weights of the topcoats were 0.099 and 0.054 g, respectively, with no measurable (micrometer) increase in overall thickness.

Significant improvement in ultraviolet reflectance was realized for all samples. As shown in Figure 7, sample 1-B was more reflective in the ultraviolet and visible than either its zinc oxide-silicate substrate (1-A) or zirconia-silicate, but less reflective than its substrate in the infrared region. With thinner topcoats the improvement in near-ultraviolet reflectance is somewhat less (Figure 8); however, infrared reflectance of this topcoated system is maintained at a level as light as the zinc oxide-silicate. Topcoating thus appears

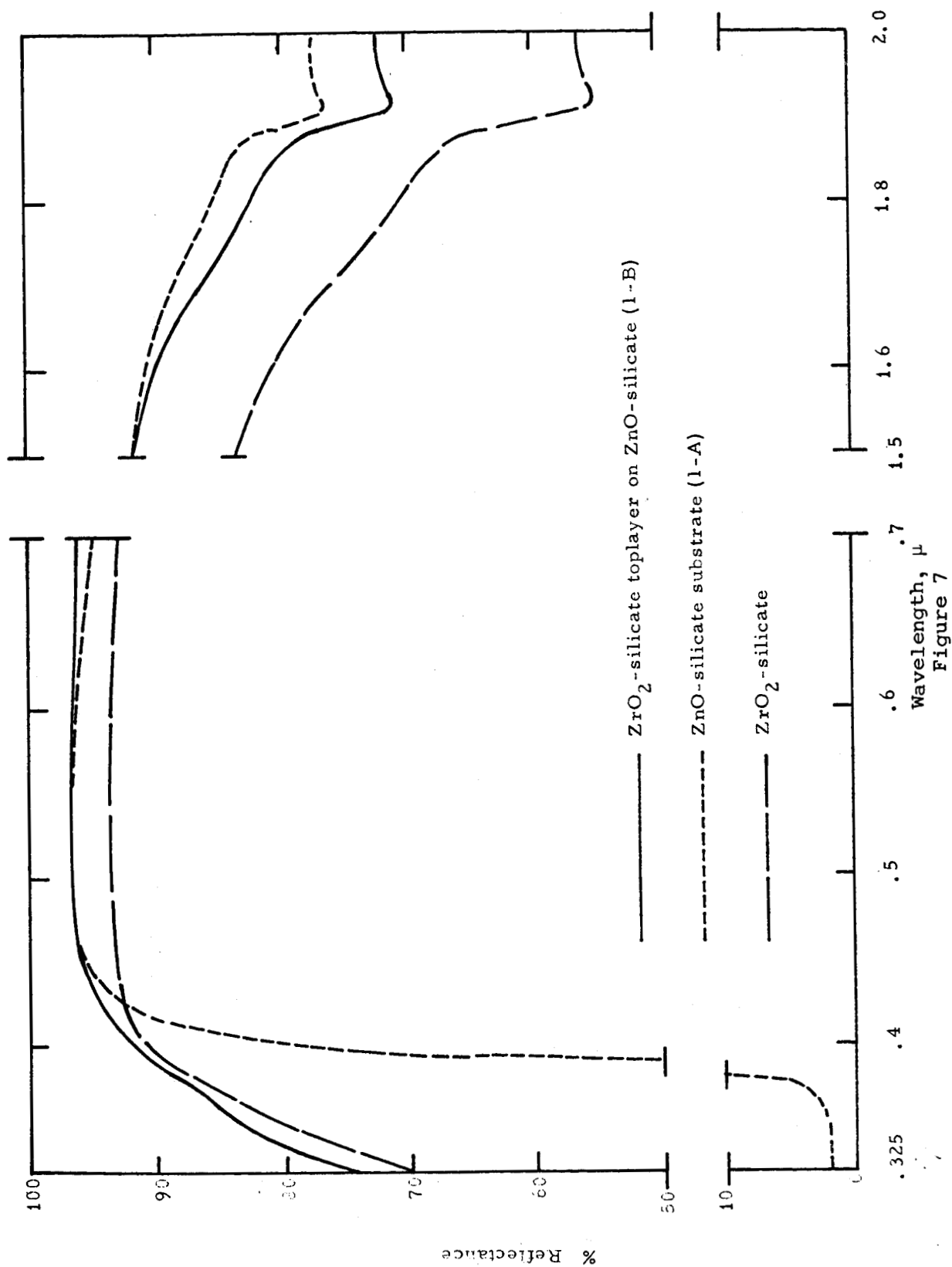
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Table 5

EFFECT OF ZIRCONIA-SILICATE TOPLAYER
ON SPECTRAL REFLECTANCE OF ZINC OXIDE-SILICATE COATING

Wavelength, μ	% Reflectance*						
	1-A	1-B	2-A	2-B	3-A	3-B	ZrO ₂ -Silicate
0.325	2.0	74.0	3.0	64.0	3.0	65.0	70.0
0.350	2.0	83.0	3.0	65.5	3.0	66.5	79.0
0.375	4.0	87.0	5.0	65.5	5.0	66.5	85.0
0.400	79.0	92.0	77.0	87.0	79.5	88.0	91.0
0.450	96.0	96.0	94.0	96.0	96.5	97.0	93.0
0.500	96.5	96.5	96.0	97.0	98.0	98.0	93.5
0.600	96.0	96.5	96.0	96.5	98.0	98.0	93.5
0.700	95.0	96.0	96.0	96.0	97.0	97.0	92.5
0.800	94.0	95.0	95.0	85.5	96.5	96.5	92.0
0.900	93.5	94.5	94.0	95.0	96.0	95.5	91.0
1.0	93.0	94.5	94.5	94.5	95.5	95.5	91.0
1.2	93.5	95.0	94.5	95.0	96.0	96.0	90.5
1.4	96.0	96.0	97.0	97.0	97.0	97.0	90.0
1.6	90.5	89.5	91.5	91.0	91.5	91.0	81.0
1.8	85.0	82.0	86.0	85.5	85.0	85.0	71.0
2.0	77.0	72.0	75.5	79.0	77.0	78.0	56.0

*versus Magnesium oxide.



EFFECT OF THICK ZIRCONIA-SILICATE TOPAYER ON SPECTRAL REFLECTANCE
OF ZINC OXIDE-SILICATE SUBSTRATE

Figure 7

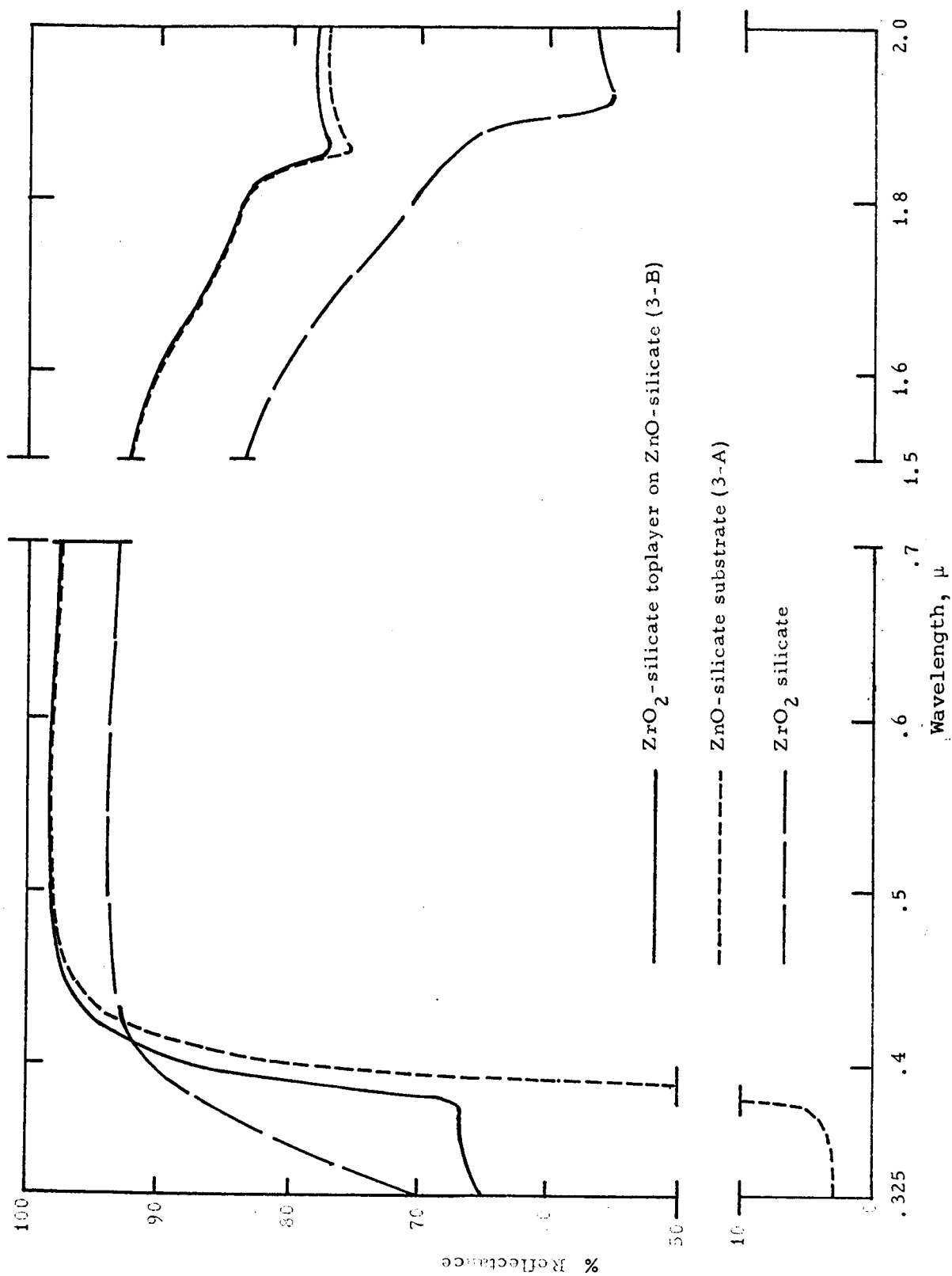


Figure 8
EFFECT OF THIN ZIRCONIA-SILICATE TOPLAYER ON SPECTRAL REFLECTANCE
OF ZINC OXIDE-SILICATE SUBSTRATE

to be a very promising method for obtaining lower α 's. A space simulation experiment is now underway to determine the stability of such a system.

IV. SILICONE COATINGS

A. Pigment Mixing Studies

One of the methods studied in an attempt to upgrade the ultraviolet reflectance of zinc oxide paints was the blending of other pigments with zinc oxide. Secondary ultraviolet-reflecting materials such as zircon and zirconia were evaluated in potassium silicate-zinc oxide systems and are discussed in Section IVB. Pigment mixing was not found to be effective in increasing the ultraviolet reflectance of zinc oxide paints. However, both experimental and theoretical considerations account for the improvement in scattering by the addition of finely divided low-index pigments to high-index pigments such as rutile.⁵ The addition of diatomaceous earths such as Micro-Cel appears to improve the scattering efficiency of the rutile by effectively optimizing the dispersion of the high-index pigment. In addition, many of the diatomaceous materials possess microporosity in the pigment

⁵Tompkins, E. H. and Ivanuski, V. R., "Coatings for the Reflection of Intense Thermal Radiation," Report No. ARF-3141-15, (Final Report), February 19, 1960 (Contract DA-11-022-509-CRD-2932).

particle, and these porosities are thought to provide additional reinforcement of scattering.

Unfortunately, the addition of microporous, finely divided extender materials (ultraviolet-reflecting secondary pigments) was unsuccessful in upgrading the reflectance of zinc oxide paints. A typical comparison between a standard zinc oxide paint (LTV-602) and a similar paint with half the zinc oxide replaced with Dicalite WB-5 is given in Figure 9. It will be noted that the WB-5 served only to dilute the zinc oxide and decreased the reflectance at wavelengths beyond 0.38μ . This same effect is noted to a lesser degree when smaller amounts of extender materials are used to replace the zinc oxide.

We can therefore treat the consideration of zinc oxide absorption in the ultraviolet in a manner similar to the utilization of carbon black pigments. That is, the addition of very small amounts of carbon black to a white pigment causes very severe decreases in reflectance in the visible regions of the spectrum. Only a few black particles dispersed throughout the white paint are needed to quickly attenuate the light by interfering with the processes of multiple scattering. Conversely, the addition of even large amounts of white pigments to a carbon black paint is ineffective in increasing the reflectance of the latter to a significant degree. The reflectance of a paint made from finely divided Teflon (Curve A) is presented in Figure 10. Curve B shows what happens to the

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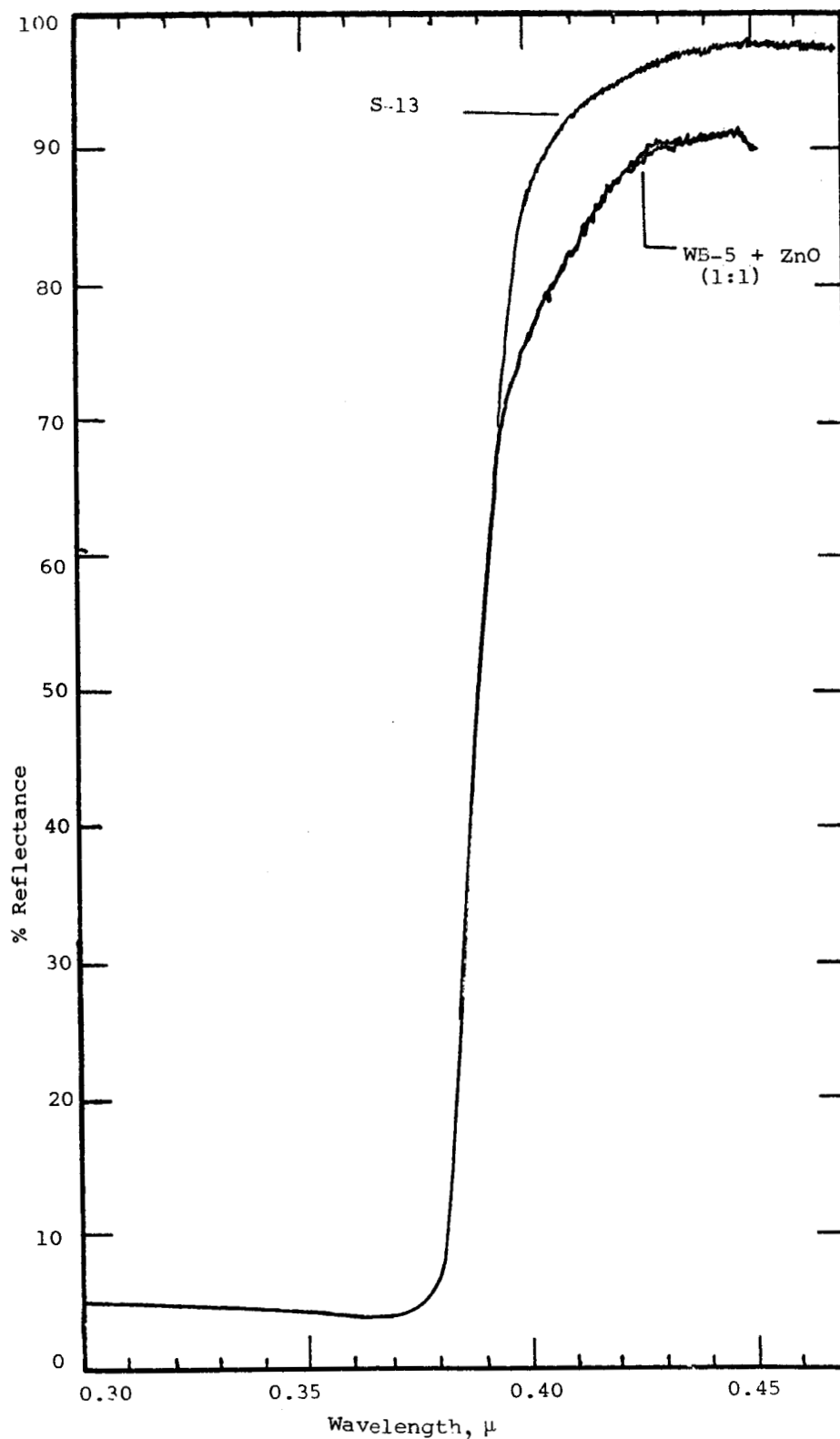


Figure 9

REFLECTANCE OF ZINC OXIDE-LTV-602 (S-13) PAINT COMPARED TO
SIMILAR PAINT WITH HALF THE ZINC OXIDE REPLACED WITH DICALITE WB-5

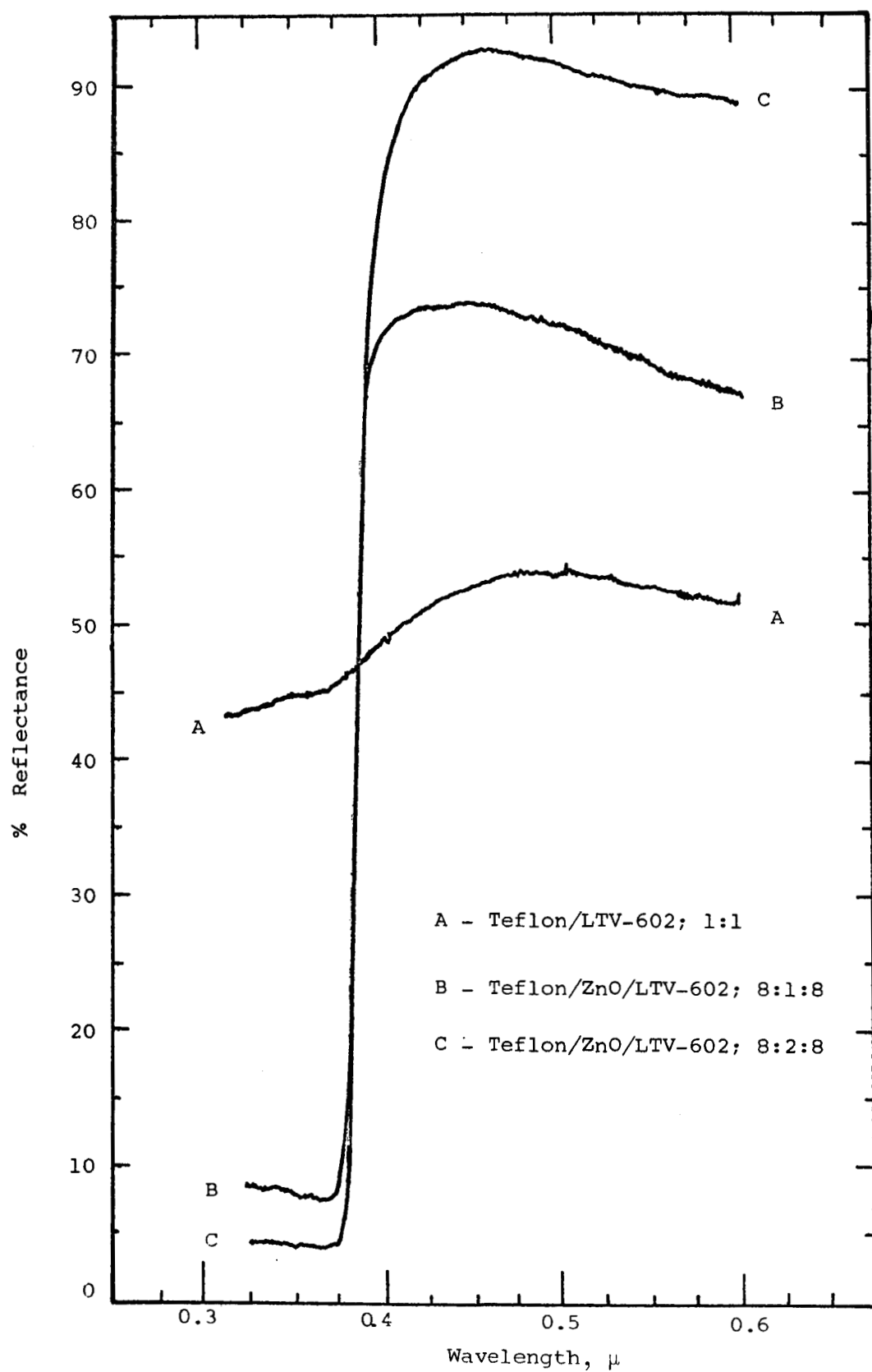


Figure 10
 EFFECT OF THE ADDITION OF ZINC OXIDE ON THE REFLECTANCE OF A
 TEFLON PAINT

ultraviolet reflectance of the Teflon paint when only a small amount of zinc oxide is added. Curve C shows the effect of doubling the amount of zinc oxide added.

B. Ultraviolet-Reflecting Topcoats

The use of tin oxide paints as thin topcoats over zinc oxide paints was discussed in the first Triannual Report (Report No. IITRI-C6014-4). It was hoped that the tin oxide would improve the ultraviolet reflection of the system at no expense either to the reflectance at longer wavelengths or to the system's stability. Not only was tin oxide found to be considerably less stable to ultraviolet irradiation than supposed, but a thin overlayer had very little effect on ultraviolet reflectance and caused a significant decrease in reflectance at longer wavelengths. Subsequent studies of overlayers have therefore been confined to better ultraviolet reflectors than tin oxide.

Free detached films of a zinc oxide-elastomeric paint (S-13) formulated at 30% PVC in General Electric's LTV-602 methyl silicone were prepared by drawing down 10-mil wet films with a Gardner knife. The films were prepared on unprimed, cleaned stainless steel plates. They were allowed to cure for 48 hr and were then carefully stripped from the steel plate. Each of four specimens prepared in this manner had a dry film thickness of 5.0 ± 0.1 mils. One specimen was used as a control. An ultraviolet-reflecting pigment was rubbed onto the backside surface of each of the remaining

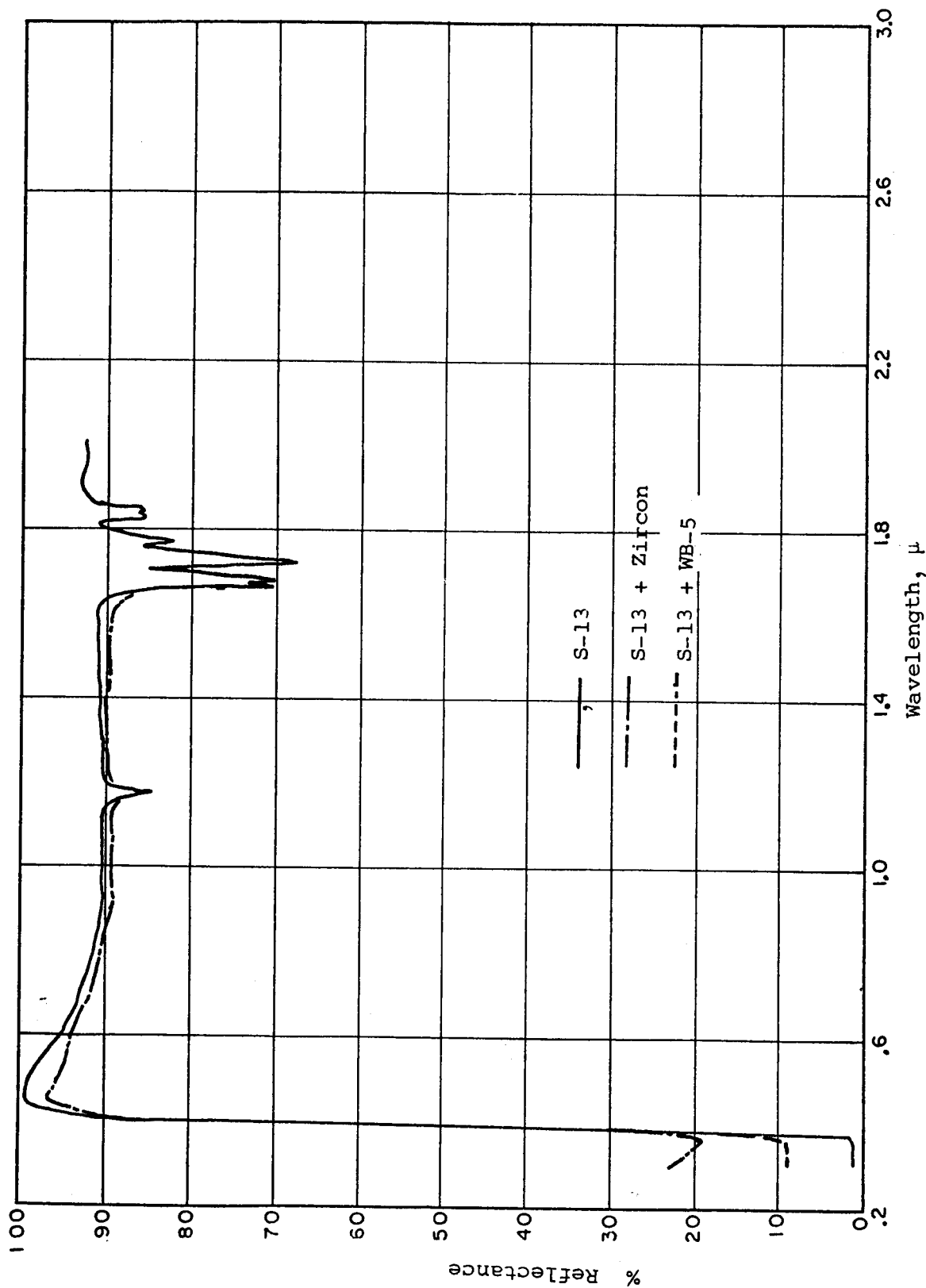
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three specimens: zircon, Lithafrax and Dicalite WB-5. These materials were gently rubbed into the surface by using excess powder and a wooden spatula. The excess powder was removed by brushing carefully with a camel's hair brush. The backside surfaces of the specimens were used in order to provide a uniform substrate for comparison purposes. The reflectances of the specimens were then obtained by affixing each to an aluminum substrate.

The spectral reflectance curves are presented in Figure 11. The Lithafrax did not affect the reflectance of the S-13 paint at either ultraviolet or longer wavelengths. The Dicalite specimen showed a slight improvement in ultraviolet reflectance of about 8% also without affecting the longer wavelengths. Only the zircon specimen showed impairment of longer wavelength reflectance, although the difference in reflectance beyond 0.7μ is believed to be due to differences in the substrate S-13 (thickness) rather than scattering.

Although not as stable to ultraviolet irradiation in vacuum as zinc oxide, both Lithafrax and zircon have been shown to possess good stabilities compared to the bulk of white pigments.⁶ It was therefore hoped that if they were thin enough, they would contribute little to the degradation and still improve the ultraviolet reflectance of the system.

⁶Mr. Harvey Brown, New Jersey Zinc Company, private communication.



REFLECTANCE OF S-13 WITH AND WITHOUT SURFACE DUSTING WITH
ZIRCON AND DICALITE WB-5
Figure 11

Zirconia was used as a topcoat in the inorganic coating studies (Section IIIC). Zirconia has a higher refractive index than zircon (2.2 versus 2.0) and would be expected to reflect more efficiently in thin coatings. Because a very thin powder film only one or two particles thick would provide the best test of ultraviolet stability versus ultraviolet reflectance enhancement, the zircon specimen (Figure 11) is currently being irradiated in a space simulation test. Thicker zircon paints are being studied as overlayers for zinc oxide-pigmented silicones.

An example of what can be accomplished is presented in Figure 12. The lower curve is the reflectance of a 3-mil Teflon sheet. The top curve is the reflectance of the system when the Teflon sheet is layered on top of a standard S-13 specimen.

Thus, it is obvious from the studies reported in Sections III and IV that any enhancement of ultraviolet reflection must be accomplished on the surface of a paint.

C. General Considerations of Paint Reflectance

1. Effect of Multiple Layers

The reflectances of two zinc oxide silicone paint specimens prepared at equal thickness are presented in Figure 13. One specimen was prepared as one coat of about 8-mil film thickness. The other specimen was prepared as four coats of the same thickness. The one-coat specimen was carefully abraded to 6.7 mils, and the multiple-coat film was abraded

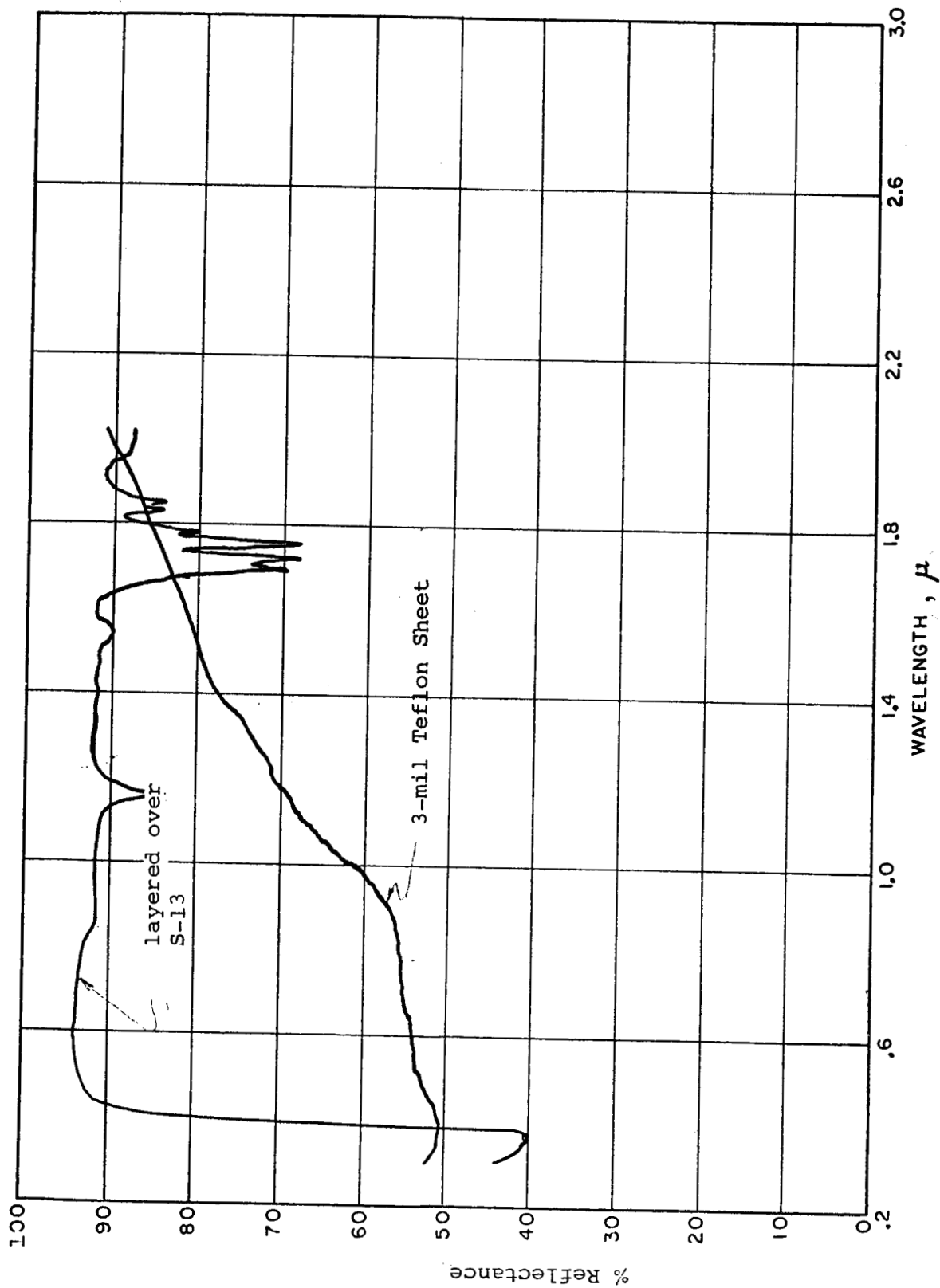
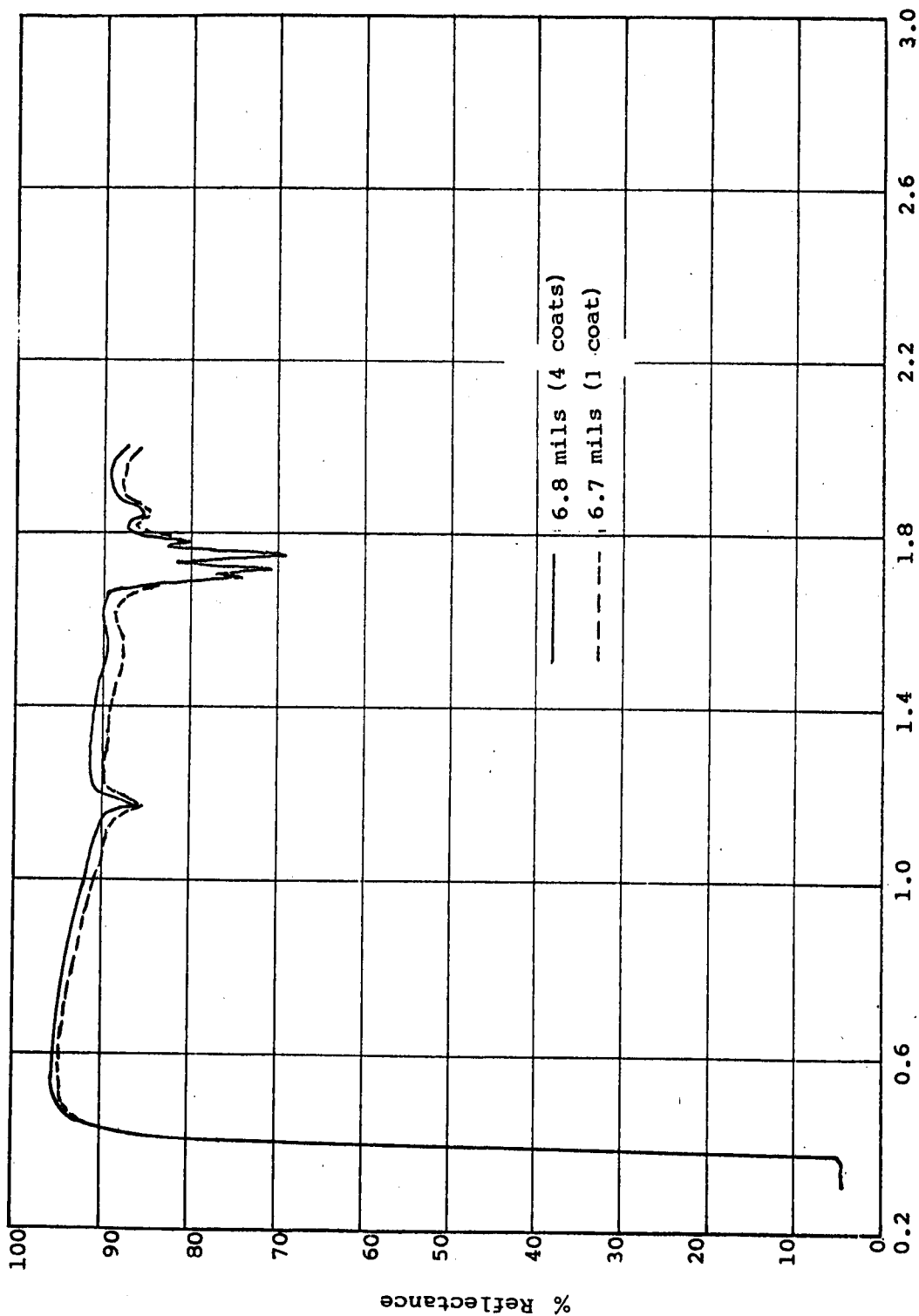


Figure 12
EFFECT OF AN OVERLAYER OF TEFLON ON AN S-13 SPECIMEN



Wavelength, μ

Figure 13

REFLECTANCE OF SP 500 ZINC OXIDE-PIGMENTED SR-80 RESIN AT 35% PVC

to 6.8 mils. This experiment was conducted in order to determine the degree of spectral reflectance which the multiple-coat paint films would exhibit compared to that of a single, equally thick coating. As shown in Figure 13, the reflectance of the multiple-coat film is 1 to 2% higher than the single-coat film in the bulk of the solar spectrum. This is attributed to refractive index changes at the interfaces of the separately cured layers. On the basis of corollary studies, it is thought that the difference of 0.1 mil in thickness of the two specimens cannot account for the difference observed in their spectral reflectance.

While the difference in spectral reflectance in Figure 13 is not great, the effect of multiple layers might become significant for coatings with higher reflectance -- that is, for coatings with solar absorptances of 0.15 or lower. For example, a 2% increase in reflectance across the spectrum would then result in a solar absorptance of 0.13.

2. Effect of Substrate Reflectance

The contribution to spectral reflectance of an unpolished, clean aluminum substrate is shown in Figure 14. The bottom curve is the reflectance of an unbacked, free detached film of S-13 (30% PVC SP 500 in LTV-602 silicone). The dashed curve is the spectral reflectance of the aluminum substrate. These curves illustrate the importance of the substrate reflectance, even for 5-mil-thick coatings.

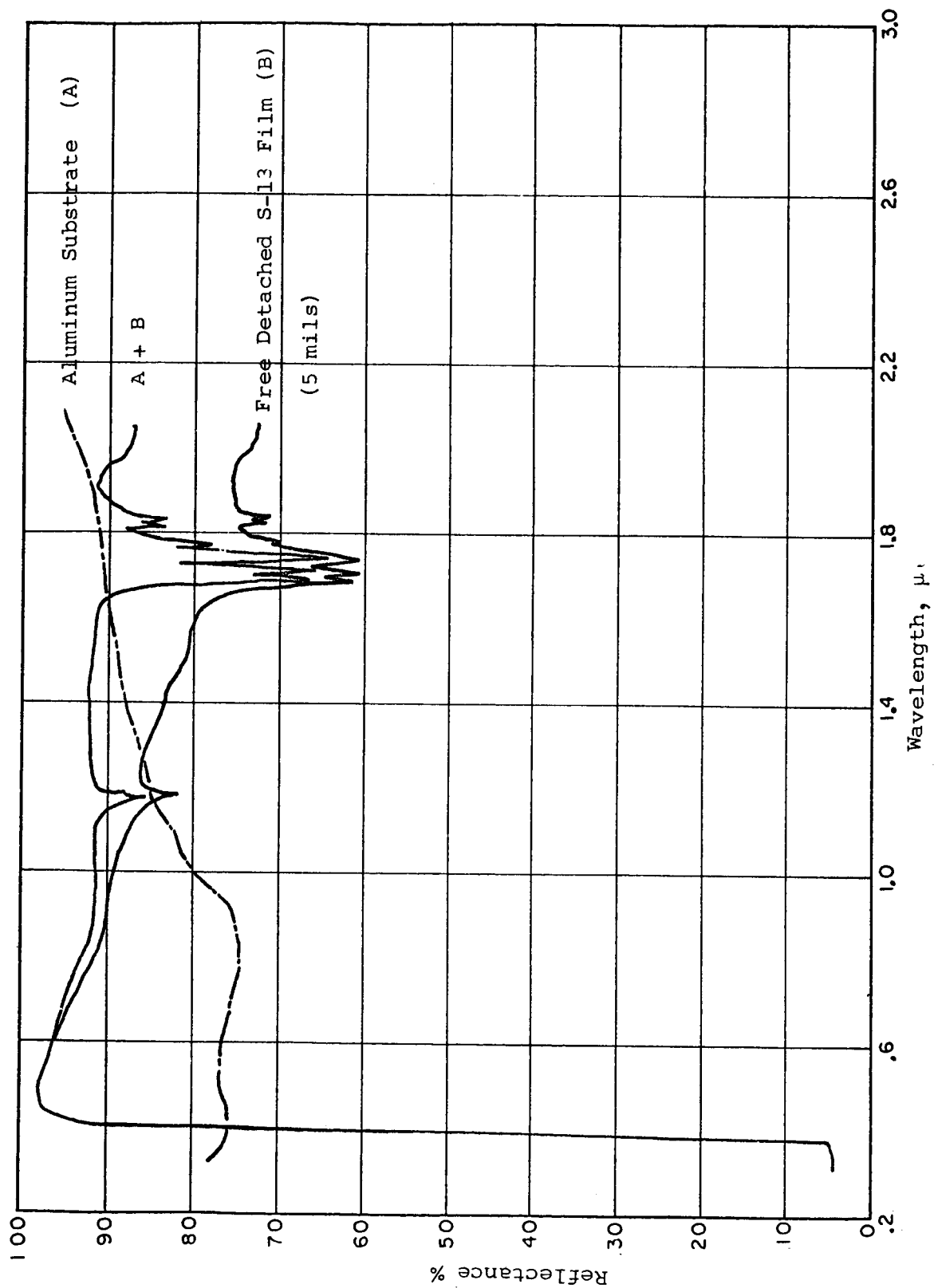


Figure 14
EFFECT OF ALUMINUM SUBSTRATE ON REFLECTANCE OF AN S-13 SPECIMEN

The uniqueness of the LTV-602 silicone is demonstrated by the ability to prepare free detached films with which reflectance studies can be made free of substrate effects. Other measurements involving hiding power and scattering studies are also suggested.

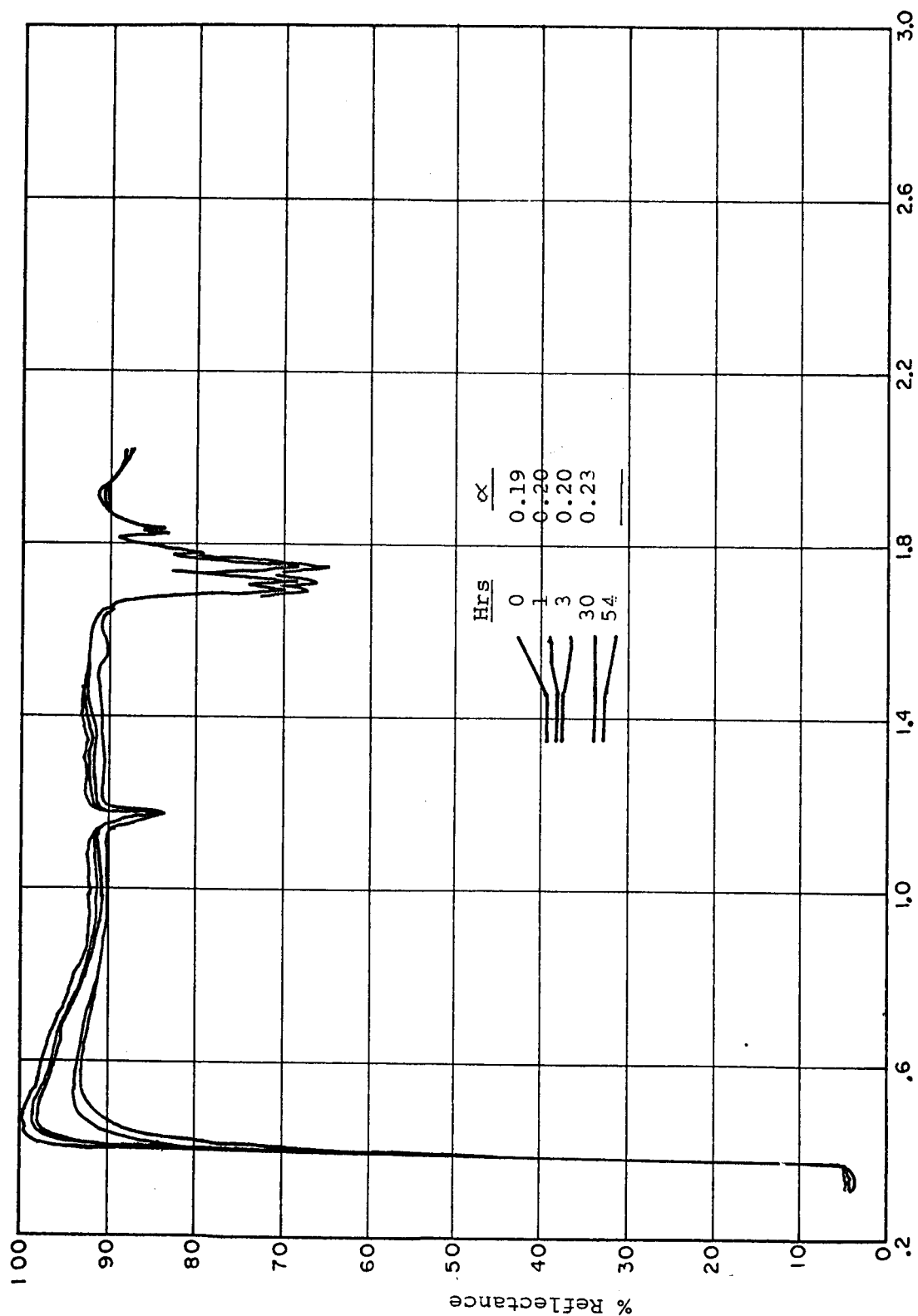
3. Effect of Grinding Time

The effect of length of grind on the reflectance of S-13 is presented in Figure 15. A basic S-13 paint was prepared and paint draw-down specimens were made after 0 (basic slurry), 1, 3, 9, 30, and 54 hr of grinding. The paints were ground in a borundum-fortified porcelain quart mill using borundum-fortified cylindrical grinding media. The surprising decrease in reflectance with only 1 hr of grinding cannot be fully explained at this time. It is thought, however, to be due to the sensitivity of zinc oxide to mechanical distortion of the crystal lattice with a subsequent shift in the absorption edge to longer wavelengths.^{1,6} The possibility of contamination is being considered; however, either silica or alumina contamination would not be expected to cause such an increase in the solar absorptance. Specimens of the various grinds are currently being subjected to ultraviolet irradiation in a space simulation experiment.

V. ANALYSIS OF ZINC OXIDE PARTICLE SIZE

Careful size (volume) distributions are being made of several commercially available zinc oxide powders. It is

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WAVELENGTH IN MICRONS
Figure 15

EFFECT OF GRIND TIME ON THE REFLECTANCE OF S-13

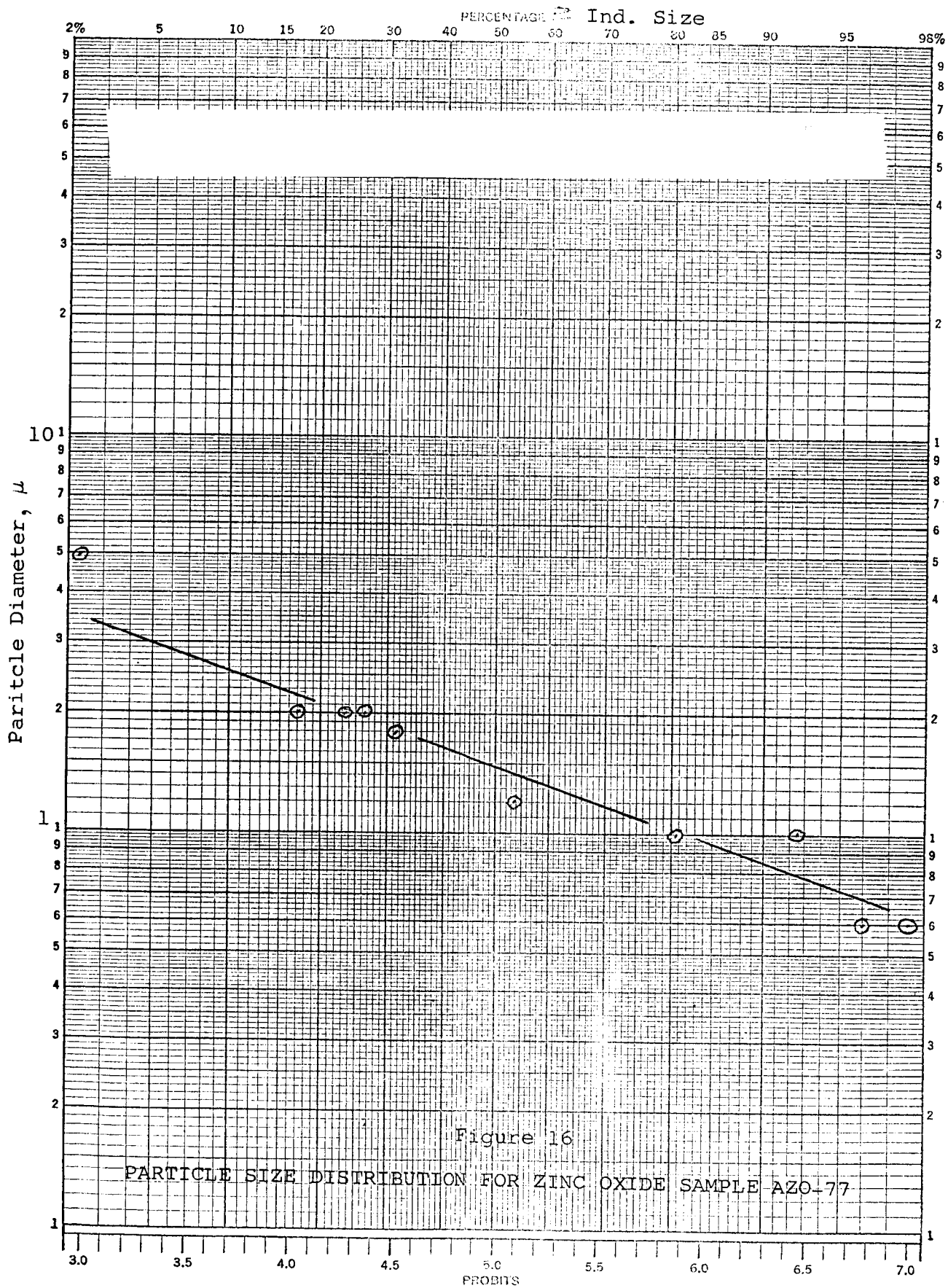
planned to mix those powders with identical or near-identical purity -- and from the same source -- in such a manner that the resultant size distribution approximates a Jaenicke⁷ distribution. This distribution will then be carefully milled into a water-white vehicle, and its spectral reflectance will be compared to otherwise identical zinc oxide paints.

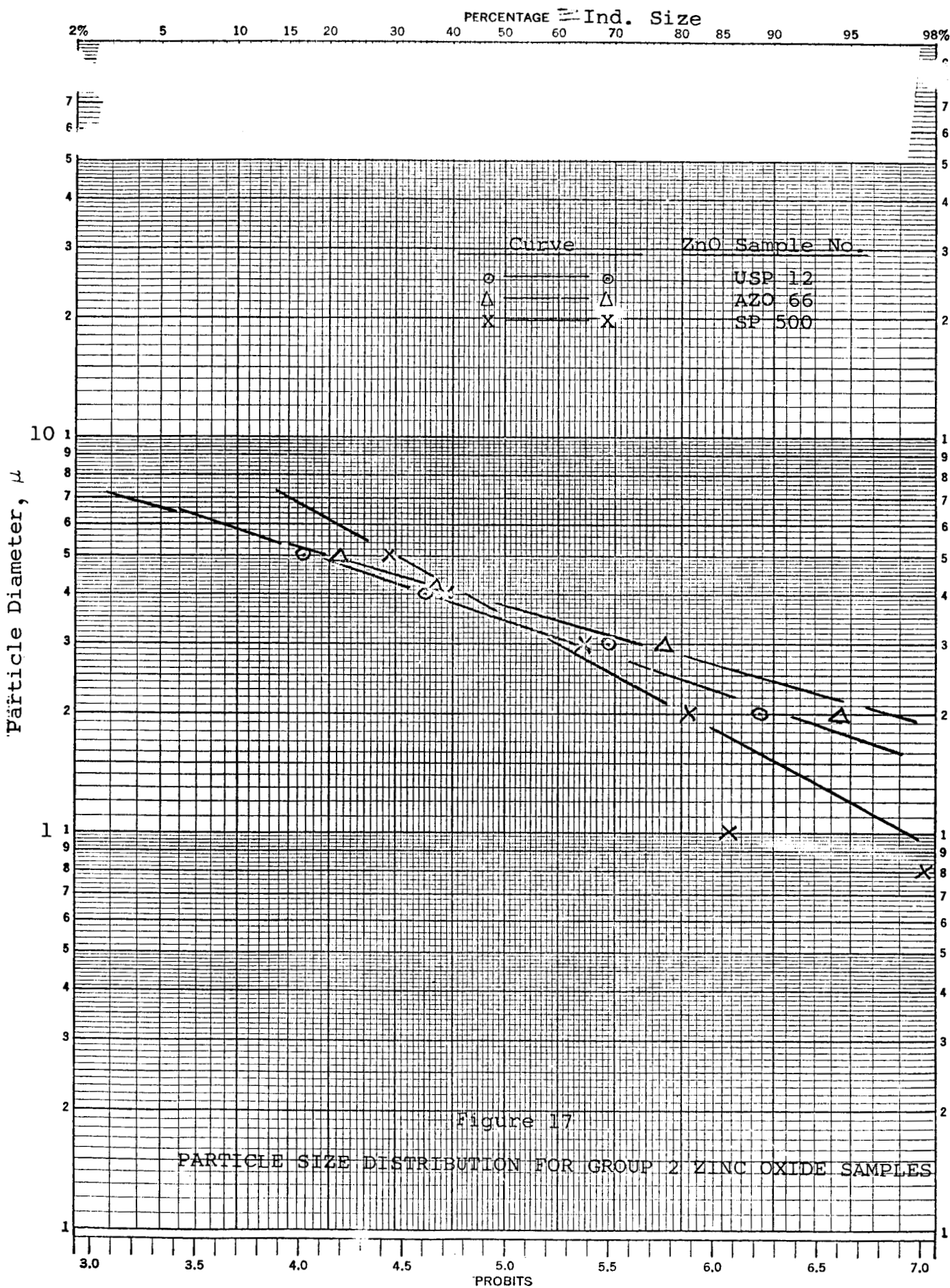
The particle size distribution curves for the zinc oxide samples listed in Table 6 are shown in Figure 16 through 19. The median diameters and standard deviations (1 std dev = 1 probit) were calculated from the log-probability plots of Stoke's equivalent spherical diameters determined with the Whitby Centrifuge Sedimentation method.⁸ Those samples exhibiting similar particle size distributions were grouped together, resulting in four distinctly different groups.

The samples in Group 4 tend to be bimodal and can be best understood by examining the distribution plots.

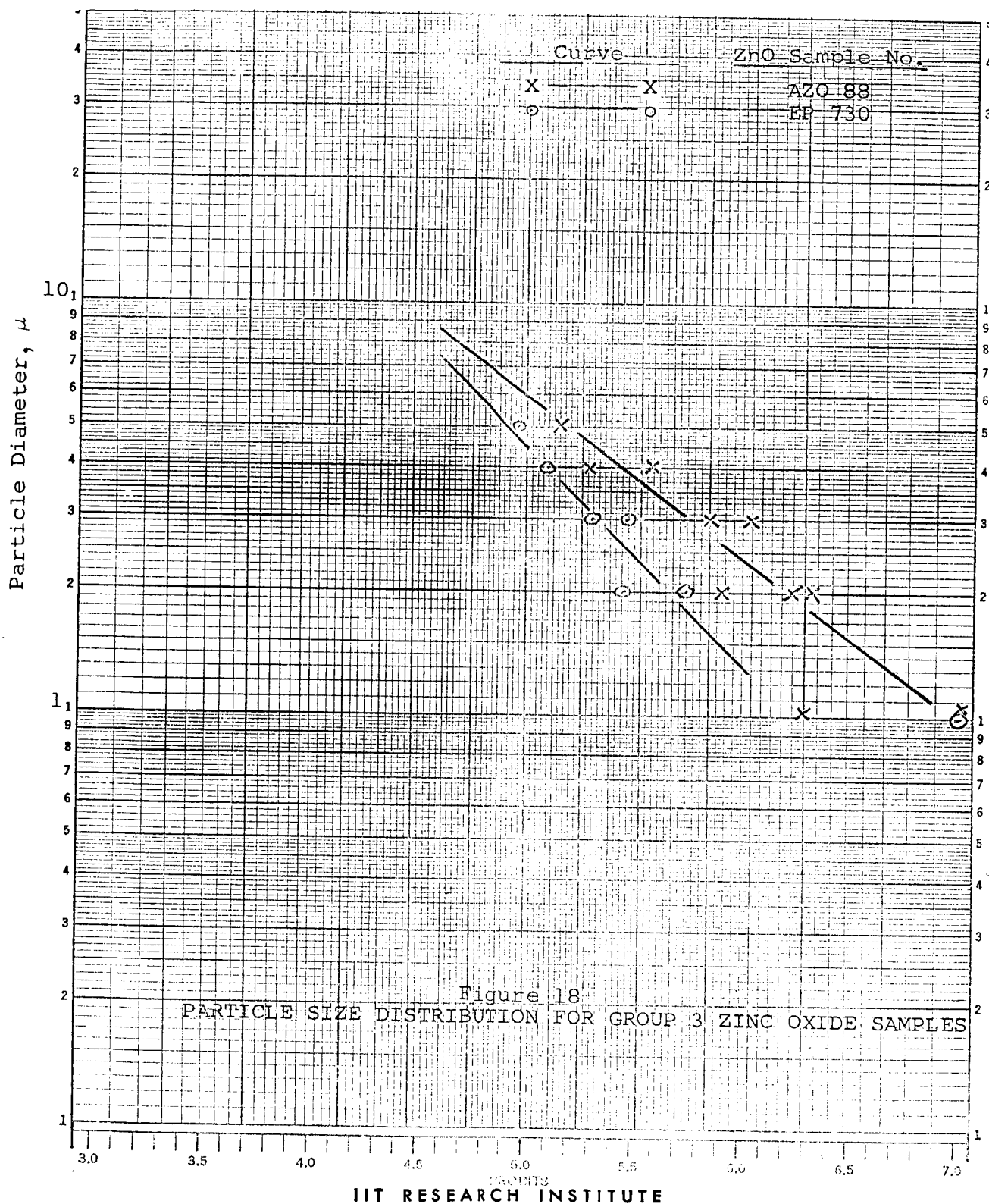
⁷Jaenicke, Walther, "Lichtstreuung und Aufhellungsvermögen Weisser Pigmente," Zeit. Electrochemie, 60, Nr. 2, 163, (1956).

⁸Whitby, K. T., "A Rapid General Purpose Centrifuge Sedimentation Method for Measurement of Size Distribution of Small Particles," Heating, Piping and Air Conditioning, June 1955.



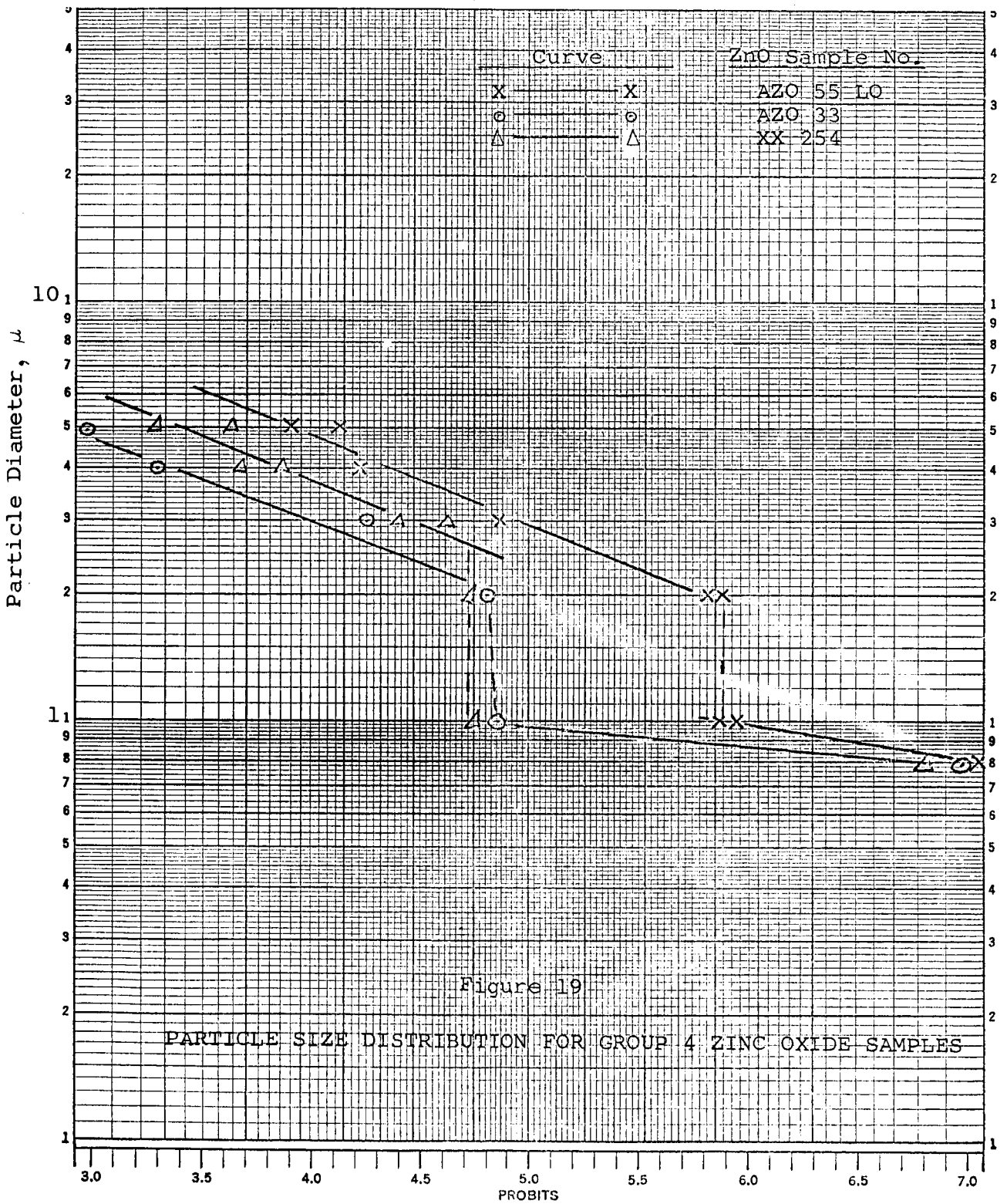


PERCENTAGE Ind. Size
 2% 5 10 15 20 30 40 50 60 70 80 90 95 98%



2% 5 10 15 20 30 40 50 60 70 80 85 90 95 98%

PERCENTAGE \geq Ind. Size



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Procedure: The zinc oxide samples were mixed with methyl alcohol (0.25 g/100 ml) containing 0.1% Aerosol OT surface-active agent. The particles were dispersed by agitating the slurry for at least 15 min in an ultrasonic bath. Additional dispersing time did not alter the size distribution for sample AZO-77. Acetone was used for the sedimentation liquid; 0.1% Aerosol OT was added also to the acetone.

A small feeding cup is used to transfer the proper amount of feeding liquid (methyl alcohol) and particles to the sedimentation liquid (acetone) in the sedimentation tube. After mixing thoroughly to give a homogeneous suspension of particles, further disturbance of the sedimentation is avoided. The height of the column of settled particles in the capillary at the bottom of the tube is recorded at a precalculated time schedule which corresponds to specific particle sizes. The centrifuge is used to hasten the sedimentation. A particle size distribution is calculated from the relative heights of the column of particles which were recorded at different times.

The centrifuge sedimentation method for determining size distributions tends to give mean sizes that are too large. Examination of Table 6 shows nearly an order-of-magnitude difference between these measurements and those reported by the manufacturer. Pigment manufacturers use both the ultraviolet-light microscope and gas absorption techniques to obtain average particle size. The gas absorption method, generally used by the industry, does not provide information

Table 6

PARTICLE SIZE DISTRIBUTION FOR ZINC OXIDE SAMPLES

<u>Group</u>	<u>Sample</u>	<u>Median Diam., μ</u>	<u>\bar{X}, Standard Deviation*</u>	<u>σ, Size Reported by Manufacturer</u>
1	AZO-77	1.5	1.5	--
2	USP 12	3.4	1.5	0.3
	AZO-66	3.7	1.5	0.2
	SP 500	3.5	1.8	0.3
3	AZO-88	5.2	2.5	--
	EP 730	4.4	2.9	5.4
4	AZO-55 LO	2.9	1.6	0.4
	AZO-33	see Fig. 4	acicular pelletad	0.2
	XX 254	see Fig. 4	acicular pelleted	1.5

*Indicates the central 70% (approximately) of the size distribution, i.e, 70% of the particles lie between $\sigma \bar{X}$ and \bar{X}/σ .

concerning the distribution of the particles. We have therefore begun electron microscope investigations of the same pigments reported in Table 6 and will relate the centrifugal sedimentation data reported in Figures 16 through 19 to average sizes determined by electron microscope counts. This is being done in an attempt to utilize the distribution plots in Figures 16 through 19 for pigment blending purposes.

VI. SUMMARY

The investigations of microbubble structures have indicated the great potential for this type of scattering system. A porous methyl silicone coating with a solar absorptance of 0.11 has been formulated by leaching a finely divided salt from the silicone matrix with water. Thus, the real limitations to the use of microbubbles as scatterer appears to be the stabilities which can ultimately be achieved with polymeric films. The principal problem currently being investigated is the possibility of enhanced degradation of the polymer matrix due to deep scattering of ultraviolet radiation. One application of highly reflecting (and stable) microporous foams is the dual ability to reflect solar energy and provide thermal insulation simultaneously.

Pigment mixing studies employing zinc oxide and a secondary, ultraviolet-reflecting pigment were generally unsuccessful in improving the ultraviolet reflectance -- and thus the solar absorptance -- of corresponding paints. In

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some instances the secondary pigment not only failed to improve ultraviolet scattering but also had an adverse effect on the scattering of zinc oxide at longer wavelengths.

Overlayers of ultraviolet-reflecting paints appear to hold some promise for decreasing the solar absorptance of zinc oxide paints. The principal problem with topcoats such as zircon, zirconia, or Lithafrax will be the competition between coatings thick enough to provide reflectance reinforcement in the ultraviolet and coatings thin enough not to detract significantly from the ultraviolet stability of the system.

The foregoing conclusions have played a large part in planning future research. For example, it is planned to more strongly emphasize ultraviolet screening investigations of potential white pigments which have not been evaluated. Also, if it is found that microporosity in polymer films enhances the discoloration of the matrix, it will be necessary to increase the emphasis on techniques to reflect the ultraviolet on the surface of the pigmented coatings. Further research in stabilizing methyl silicones against ultraviolet radiation in vacuum is also suggested.

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